REVIEW OF LITERATURE ON HEALTH HAZARDS OF FLUORINE AND ITS COMPOUNDS IN THE MINING AND ALLIED INDUSTRIES

BY S. J. DAVENPORT AND G. G. MORGIS

* * * * * * * * * * **Information Circular 7687**

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S. J. Davenport[1] and G. G. Morgis[2]

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INTRODUCTION

The increased consumption and importation of fluorspar and cryolite (1)3/ in recent years, and especially the addition of fluorine compounds to drinking water in the United States, have aroused renewed interest in the properties of such compounds and possible health hazards incident to their use. It has been suggested that the issuance of a revision and elaboration of Information Circular 7311, The Hazards of Hydrogen Fluoride Poisoning in the Mineral and Allied Industries, which has been out of print for some time, would be opportune.

Fluorine minerals have been known since the Middle Ages. Fluorine was isolated in 1886 by Moisson (2).

Up to 1947 the field of fluorine chemistry was only a small segment of the chemical industry. However, fluorine chemistry can hardly be called new. Many inorganic fluorides, such as fluorspar, boron trifluoride, fluosilicates, cryolite, and sodium fluoride, have been commercially important for years (3).

Before World War II fluorine was generated in gram quantities with difficulty and could not be purchased at any price; but by 1947 the scientific and technologic advancement in its generation had been so spectacular that a large part of the program of the Division of Industrial and Engineering Chemistry at the 110th Meeting of the American Chemical Society was devoted to a Symposium of Fluorine Chemistry (3).

SUMMARY

Fluorine, one of the most active elements chemically, ranks 17th in abundance among the elements of the earth's crust. The principal fluorine-bearing minerals that are used in large scale industrial processes are fluorite or fluorspar, cryolite, and sedementary phosphate rock.

Fluorine and its derivatives are used industrially in numerous processes as: Plastics, germicides, fungicides, insecticides, pharmaceuticals, anesthetics, dyes, stable solvents, fire-proofing material, resins of innumerable applications, separation of uranium isotopes by gaseous diffusion, fermentation of alcohol, insulators in high-voltage electrical and X-ray fields, and in the chemical laboratory for certain types of analytical work. In addition to the use of fluorides in large-scale industrial processes, they are used on a small scale in about 31 technical processes.

A relatively new use for salts of hydrofluoric acid is the addition of controlled amounts of fluoride chemicals to drinking water supplies that do not contain fluorine.

3/ Underlined numbers in parentheses refer to items in the Bibliography at the end of the report.

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Some of the more important industries where there are possibilities of exposure to fluorides are in smelting (production of aluminum and beryllium), petroleum industries, and manganese foundries.

The physical and toxic properties of 73 compounds of fluorine are summarized.

The discussion of the toxicity of fluorine covers effects on plants, animals, and man.

The hazards of hydrogen fluoride, first-aid treatment, and prevention and control of exposures to hydrogen fluoride are discussed. Arguments for and against fluoridated public water supplies are presented.

OCCURRENCE OF FLUORINE

As fluorine is one of the most active elements chemically, it does not occur free in nature. However, it is a rather common element, ranking 17th in abundance among the elements of the earth's crust (2). Fluorine compounds are found frequently in gases from volcanoes and fumeroles. Igneous rocks usually contain this element in varying amounts (0.01 to 3.36 percent), and its compounds have been found widely distributed in many types of rock formation. It has been found in some British coals in amounts ranging from nil to 175 p.p.m. Apparently the fluorine is present in coal in the form of fluorapatite (4).

The first published observation of the presence of fluorine in coal appears to have been that regarding the disfigurement of glass bottles, which were etched by fluorine compounds derived from coals used in an annealing kiln. This was published in the Annual Report of the Fuel Research Board for the year ended March 31, 1934 (5). Crossley quoted Lessing as stating that severe corrosion of the porcelain fillings of a gasworks scrubber had been found by him to be due to fluorine compounds originally present in the coals.

Small quantities of fluorine occur in some of the micas, in topaz, and in tourmaline. Traces are present in plants (6), in the soil, in sea water, in some mineral springs, and in some drinking waters; it is also found in bones, teeth, blood, and milk of animals; although it is said not to be a constituent of the human body at birth (7), but Marcovitch and Stanley (8) found the fluorine content of rats at birth to average 4.36 p.p.m.

Fluorspar, a natural calcium fluoride, is found in cavities in granite rocks, veins of tin ores, sandstone, and most abundantly as an associate of lead ore in veins traversing limestone (9).

Phosphate rock contains fluorine as an impurity (10).

USES OF FLUORINE-BEARING MINERALS

The principal fluorine-bearing minerals that are used in large-scale industrial processes are fluorite or fluorspar (CaF_2), cryolite (Na_3AlF_6), and sedimentary phosphate rock (11).

Fluorspar

Fluorspar is highly important, and in many cases indispensable, to such basic industries as steel, aluminum, chemical, and ceramic. Of many substitutes tried,

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none has proved nearly as effective as fluorspar. It is also the raw material from which nearly all other fluorine compounds are derived (12). It is a nonmetallic mineral mass containing enough fluorite (CaF_2) to be of commercial interest (13).

Industrial grades of fluorspar prepared for the consumer normally contain 85 to 98 percent fluorite. Fluorite contains 51.1 percent calcium and 48.9 percent fluorine.

The acid grade of fluorspar is used almost exclusively to make hydrofluoric acid by reaction with sulfuric acid. This is the first step in the manufacture of numerous products, such as artificial cryolite to reduce aluminum from its oxide, Freon 12 for refrigeration, and aerosol for certain insecticides (12).

The bulk of the fluorspar marketed in the United States, and most of that imported, is used in the steel industry, principally in the basic open-hearth process. The quantity used per ton varies between plants; a normal average is about 6.5 lb. per ton.

Fluorspar is used as a flux to make ferroalloys, nickel, brass, basic refractories, and bessemer steel. It is also used to refine several of the nonferrous metals (13).

Cryolite

Cryolite, a double fluoride of aluminum and sodium ($3NaF.AlF_3$), contains 12.8 percent Al, 32.6 percent sodium, and 54.3 percent fluorine. The principal use of cryolite is in the aluminum industry as electrolyte in reducing alumina to the metal. It is used also in the zirconium and rare earths' industries and in the manufacture of calcium carbide. It is used in the enamel and glass industries, as a binder for some abrasives, and as insulating material having special dielectic properties (13).

Phosphate Rock

All types of commercial phosphate rock produced throughout the world contain fluorine in quantities ranging from approximately 0.4 to 4.2 percent. A considerable part of the domestic supply of fluosilicates and fluosilicic acid is derived from the fluorine volatilized during the manufacture of ordinary superphosphate (14).

USES OF FLUORINE-BEARING COMPOUNDS

In Industrial Processes

Waggaman (15) has called attention to the industrial value of fluorine and its derivatives as follows:

> It is a far cry from a corrosive chemical, such as hydrofluoric acid, to the many useful products for which it is responsible. Moreover, many of the industries in which fluorine plays such an important part seem about as far apart as light and darkness. The average person can see little relation between a roaring steel furnace discharging metal at 3,000° F. and a refrigerating unit operating at a temperature far below the freezing point. Neither does there appear to be any connection between glass and high-octane motor fuel, or the enameled furniture in a smart New York beauty parlor and the insecticides that protect our armed forces in the jungles of New Guinea.

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Yet fluorine in one form or another is doing a magnificent job in manufacturing these as well as many other products. A chemical devil has been tamed and trained to serve our needs in war and peace.

The fluorines are used in the fermentation industries, particularly in the fermentation of alcohol, where in suitable doses they inhibit the accessory fermentations caused by bacteria without acting on the yeast. The fluorides are likewise utilized in the brewery, especially ammonium fluoride and aluminum fluoride. The utilization of too strong concentrations has, in the manufacture of beer, led to beverages rich in fluorine susceptible of producing toxic reactions (16).

Wood is impregnated with solutions of fluorides and fluosilicates to destroy the various ligneous fungi and also termites (for example, impregnation of telegraph poles). Sodium fluoride is used to conserve glue and combined with casein and fluosilicic acid to disinfect skins and leathers (16).

New and recent uses for fluorine compounds have been found in plastics, germicides, fungicides, pharmaceuticals, anesthetics, new and useful dyes, lubricants, tanning agents, stable solvents, fireproofing materials, and resins of innumerable applications (15).

Perfluoroheptane has been used in a process for separating uranium isotopes by gaseous diffusion (17). Sulfur hexafluoride (SF_6) is being used as an insulator in the high voltage electrical and X-ray fields.

The fluorocarbon plastic Teflon, made by the polymerization of tetrafluoroethylene, has been especially successful in generating and handling fluorine (3). Tetrafluorethylene resin is the "queen of the resins" (18) for corrosive service because it is inert to almost everything. It is attacked only by molten alkali metals and by fluorine at elevated temperatures and pressures.

One of the most important compounds of fluorine is hydrogen fluoride. Medium and weak solutions of hydrofluoric acid in water dissolve every metal except gold and platinum. It is used in etching glass, in manufacturing sodium and ammonium fluoride, and in the chemical laboratory for certain types of analytical work. Through the medium of hydrofluoric acid a series of complex organic compounds, grouped under the trade name "Freons", have been developed. The most widely used member of this group is dichlorodifluoromethane (F-12). It is an almost ideal and relatively cheap refrigerant and has served to stimulate the household refrigeration and air-conditioning industries. As a result of the successful development of Freon, hydrofluoric acid and its derivatives are being used to manufacture dyes and solvents, in color photography, in insulating and cooling dielectics, and in building up and breaking down organic compounds, thus yielding new and valuable end products (17).

High octane gasoline, so necessary for use in giant bombers, swift fighters, and other types of mechanized equipment, is produced from petroleum through the medium of pure anhydrous hydrofluoric acid. It reacts with organic materials, rearranging the molecules and yielding products to suit certain industrial needs. The broad field of usefulness thus opened up for this chemical and its derivatives is indicated by the fact that in 1945 one of the largest chemical companies was offering over 35 compounds of hydrofluoric acid having commercial applications (17).

Many complex ions in which fluorine is involved are known. The iron-fluorine complex is the basis for the use of potassium difluoride to remove rust spots from clothing and similar materials and is thus used in the laundry industry.

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In Technical Processes

In addition to the uses of fluorides in large-scale industrial processes, their use on a small scale in technical processes are listed in table 1, prepared by Greenwood (19).

TABLE 1. - Uses of fluorine compounds in technical processes

1.	Binder for emery wheels	CaF_2
2.	Bleaching of cane for chair seats	SF_6
3.	Bleacher in laundries	Na_2SiF_6
4.	Cleansing graphite	HF
5.	Coagulating rubber	Na_2SiF_6; $MgSiF_6$
6.	Decolorizing of glasses	Na_2SiF_6
7.	Disinfection of hides and skins	H_2SiF_6
8.	Disinfection of hose and tanks in breweries	H_2SiF_6; NH F.HF
9.	Electrolytic manufacturing of beryllium	Na_2SiF_6
10.	Fixing of tannin on cotton in dye works and printing works	SbF_3
11.	Flotation of fluorspar and quartz	CaF_2
12.	Flotation of lead-zinc-fluorspar ores	CaF_2
13.	Flux	Na_3AlF_6; Na_2SiF_6; CaF_2
14.	Glass etching	HF; NH_4F
15.	Hardening cement	$MgSiF_6$; $ZnSiF_6$
16.	Insecticidal powders	NaF
17.	Making glue, paste, and adhesives	HBF_4
18.	Making synthetic stones	Sundry compounds
19.	Optical industry	CaF_2
20.	Preserving wood (building) timber, telegraph poles	NaF; ZnF_2; $MgSiF_6$
21.	Recovery from phosphate plant	H_2SiF_6; $PbSiF_6$
22.	Refining mineral oils	SO_2F_2; SF_6
23.	Refrigerating industry	CCl_2F_2; $C_2CL_2F_4$
24.	Removing sand from castings	HF
25.	Rust removal from steel and iron	HF
26.	Silicate analysis and condensing agent in laboratory.	HF
27.	Silk dyeing	HF
28.	Synthetic production of cryolite	CaF_2
29.	Treating anthracite for making gas coal	HF
30.	Window cleaner	H_2SiF_6
31.	Wood staining	CrF_3

In Drinking Water Supplies

A relatively new use for salts of hydrofluoric acid and one offering possibility of an enormous increase in the demand for this acid is the addition of fluoride chemicals to drinking water supplies that do not contain fluorine. It has been estimated that such addition to municipal waters would increase the annual consumption of fluorine salts by many thousands of tons (17).

D. J. Galagan, United States Public Health Service, in a letter August 18, 1953, reported the following breakdown of the number of people using the different types of fluoride chemicals in their water supplies, as of January 1, 1953:

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Chemical Used	Population
Sodium fluoride	5,000,000
Sodium silicofluoride	8,400,000
Hydrofluosilicic acid	1,500,000
Hydrofluoric acid	100,000

Summary

As a partial summary of the uses of fluorine-bearing compounds the following list issued by the State Health Department of New Jersey (20) is included:

Fluorine-bearing compounds may be used:

1. By launderers to neutralize the alkali that cannot be rinsed out of cloth.
2. In ceramic processes fluorides as an ingredient in enamel, as a flux and opacifier, and in pottery glazes.
3. By breweries and distilleries to disinfect fermentation equipment.
4. In the electrolytic production of aluminum.
5. In welding fluxes and coatings on welding rods.
6. In the glass industry to etch and polish glass.
7. In magnesium production as inhibitors and fluxes.
8. To convert rock phosphates into fertilizer.
9. In producing highly stable fluorinated refrigerants.
10. In some foundry processes to clean castings by dipping them into hydrofluoric acid.
11. In producing steel, nickel, copper, gold, and silver.
12. Other general industrial uses: Binder for emery wheels; to bleach cane for chair seats; cleaning graphite; coagulating rubber; disinfecting hides and skins; electrolytic manufacture of beryllium; making glue, pastes, and adhesives; making synthetic stones; optical industry; preservative for timber; refining mineral oils; rust removal from iron and steel; silicate analysis; silk dyeing; treating anthracite for making coal gas, window cleaner, wood staining, insecticides, and rodent poisons.

FLUORINE EXPOSURES

In an investigation by the Adult Hygiene Division of the Ohio Department of Health, assisted by the personnel of the Works Projects Administration in Ohio (21), contact with fluorine and its compounds was indicated in the occupations given in table 2.

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TABLE 2. - Occupations in which contact with fluorine and its compounds is indicated

Autoclave men (chemicals).	Laborers (electric fixtures, tin and enameled ware, foundries, glass factories).
Beaders (tin and enameled ware).	Machinist (storage batteries).
Blowers (glass factory).	Mill men (distilled malts and wines).
Brewmasters (distilled malts and wines).	Mixers (tin and enameled ware, fertilizer factories, glass factories).
Burners (tin and enameled ware).	Pit cutters (fertilizer factories).
Car men (fertilizer factories).	Platers (electrical machinery, metal furniture, printing, brass factories, storage batteries).
Chemists (distilled malts and wines).	Pressers (glass factories).
Den men (fertilizer factories).	Processors (electrical machinery).
Dippers (tin and enameled ware).	Rimmers (tin and enameled ware).
Elevator men (fertilizer factories).	Rug cleaners (dry cleaning and dyeing).
Enamel makers (tin and enameled ware).	Smelters (tin and enameled ware).
Etchers (other manufacturing plants; electrical machinery).	Spongers (tin and enameled ware).
Evaporator men (chemicals).	Spotters (dry cleaning and dyeing).
Fermenting cellar workers (distilled malts and wines).	Sprayers (tin and enameled ware).
Foreman (distilled malts and wines; jewelry).	Storage men (distilled malts and wines).
Frosters (electric fixtures).	Tinners (electroplating).
Furniture cleaners (dry cleaning and dyeing).	Warehouse men (distilled malts and wines).
Hot galvanizers (electrical machinery).	Washing-machine operators (laundries).
Insecticide mixers (soap factories)	Weigh-car operators (tin and enameled ware).
Kettle cars (distilled malts and wines).	

A detailed discussion of exposure to fluorides in some of the more important industries follows:

Smelting Industry

Production of Aluminum

Fluorides may pollute the inside of the plant and the surrounding atmosphere in the reduction of aluminum. The process employed to produce metallic aluminum is virtually the same as that described in the original Hall-Heroult (22) patents of 1886-1888. The aluminum made today is a result of the electrolysis of alumina (Al_2O_3) dissolved in a bath of molten cryolite. Carbon electrodes dip into the fused salt bath container in a carbon lined steel tank or "cell."

Aluminum oxide has a heat formation of 378,000 calories and therefore is one of the most difficult of the common metallic oxides to decompose (22). Davy (23) first attempted the reduction in 1807, using metallic sodium or potassium. Theoretically, alumina can be reduced by carbon, but, as a temperature of 2,100° C. must be attained for the reaction to go on at a reasonable speed, major difficulties would be encountered (the metal boils at 1,800° C.). In 1864, Bunsen found that the fused chloride

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could be decomposed, but it remained for C. M. Hall, in 1886, to invent the present process whereby alumina is dissolved in an igneous bath, composed mainly of cryolite, and then electrolyzed (23).

A standard electrolytic cell consists of a steel shell or pot constructed of steel plate and lined with baked carbon 6 to 10 inches thick (this constitutes the cathode of the system). Cylindrical carbon anodes are suspended from the anode bus bar. Each pot consumes up to 50,000 amperes at a potential of 5 to 6 volts. Ordinarily there are 30 to 100 of these pots in series, making a total potential drop of 200 to 600 volts. The igneous bath, maintained at about 950° C., is composed of cryolite containing calcium and alumina fluoride. It has a specific gravity of about 2.1 and will dissolve up to 20 percent of aluminum oxide, although it is usually maintained at 2 to 5 percent. As electrolysis proceeds, molten aluminum collects in the bottom of the container in a layer 1/2 to 5 inches thick, from which it is tapped as needed. An 8,000-ampere cell will make about 40 pounds of metal per hour; a 30,000-ampere cell, about 150 pounds. Theoretically about 5 kilowatt-hours are required to produce a pound of aluminum, but actually 12.5 to 13 kilowatt-hours are necessary.

According to Feil (24), the principle of the method is the decomposition, under the influence of the heat developed by the electric current, of the cryolite and its combination with the silica of the carbon of the electric arc to form a gas - silicon fluoride - which in turn is transformed almost immediately into fluosilicic and hydrofluoric acid. The hydrofluoric acid thus produced may affect not only the plant personnel but persons within a radius of several miles.

F. C. Frary, Director of Aluminum Research Laboratories, Aluminum Co. of America, in a letter July 26, 1945, said the principle of the method is the decomposition by the electric current of the alumina dissolved in the molten cryolite. A certain amount of the molten cryolite evaporates or is carried away in the form of a fine fume, and some of it is hydrolyzed by the moisture of the air to produce hydrofluoric acid, which escapes into the air, and sodium fluoride and alumina, which remain in the bath. Possibly traces of silicon tetrafluoride may be formed from the silica in the raw materials. Practical experience has shown that the plant personnel are not injured by the small amounts of hydrofluoric acid and cryolite fumes present in the air in most plants. Obviously, persons outside the plant would not be affected by the highly diluted gases that would reach them.

Although the bath is not decomposed by an electric current unless the voltage is excessively high, there is a certain constant loss of fluoride owing to volatilization. It is reported that liberation of hydrofluoric acid in a aluminum reduction works is revealed by the slight etching of the glass windows by this gas (24); this same indication of the presence of hydrofluoric acid in the atmosphere may be noticed sometimes in the vicinity of aluminum plants.

The principal exposure to fluoride poisoning in aluminum plants is in working around the pots - adding the charge, changing electrode connections, renewals, and similar operations. When enclosed pots are used the doors of pots must be opened for a short period at regular intervals. When the doors are opened wide, the hot air currents generated by the hot bath carry most of the fumes out into the room, unless each pot is properly ventilated, where the workers are exposed until the fumes are carried away by ventilating currents and discharged through roof monitors.

In plants with or without mechanical ventilating systems, large quantities of fumes may be discharged from the roof monitors and from the stacks if the latter are

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not provided with collecting or washing equipment. Some of these fumes descend to the ground level and are deposited on the vegetation within a certain radius of the plant, in accordance with the prevailing direction of the air currents, and may constitute a hazard to animals eating the vegetation.

Production of Beryllium

The economic importance of beryllium has led recently to its increased production and use. Opportunities for exposure to beryllium fumes and dust are fairly numerous in the industry in virtually all stages of beryllium production and in the manufacture of beryllium oxide and its subsequent use in the copper-beryllium alloys; however, there has not been a great deal of experimental investigation of the health hazards, probably owing to the comparatively small number of workers engaged and to the conflicting nature of the experimental data available in the literature on the toxicity of beryllium.

In 1936, Gelman (25) stated that the few experiments that had been made on the action of beryllium and its compounds were intended principally to determine the chronic action of beryllium introduced over a considerable period in small oral doses in the form of beryllium carbonate or chloride. He mentioned only two investigations in which an attempt was made to reproduce industrial conditions.

In the first of these, reported by Weber and Engelhardt (26) in 1933, it was noted that the nature of the illnesses of the workers exposed to various fluorides, among them beryllium oxyfluoride, produced during the foundry process of beryllium extraction recalled to them the picture of poisoning by corrosive gases (chlorine, phosgene). This picture led them to conclude that the important toxic element was gaseous hydrogen fluoride. They proved experimentally that the dust of sodium siliceous fluoride and siliceous flux is highly irritating to the respiratory tract and has a toxic effect. Barium fluoride and beryllium oxide were much less irritating, and inhalation of their dust caused virtually no observable disturbance to the health of the animals or any pathological-anatomical changes in the lungs. The authors (26) concluded that the question of the origin of the illnesses of workers in the foundry had not been clarified, largely because they were unable to use the vapors of beryllium oxyfluoride in their experiments.

From his own analysis of the clinical phenomena and conditions present during the foundry method of extracting beryllium from its fluorides, Gelman (25) concluded that the toxic effect was due to the vapors of beryllium oxyfluoride and that their special physical condition (great dispersion) explained their characteristic toxic effect upon workers at a distance (even in the open) as well as upon those close to the source of the vapors.

According to an article published in 1938 by the International Labor Office (27) the products utilized to obtain pure Be are beryl ($BeO\ Al_2O_3 6SiO_2$) and sodium fluosilicate (Na_2SiF_6). The Industrial processes are roughly grouped as follows:

(a) Crushing and pulverizing beryl and sodium fluosilicate, which liberates dusts, especially during manipulation.

(b) These products are treated in kilns at 680° to 750° C., producing after a series of chemical reactions a sticky mass resulting from a mixture of fluorides (Na_3BeF_4 + Na_3AlF_6 + AlF_3, etc.). Gaseous products are given off during fusion (among others silicon fluoride - SiF_4).

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(c) The agglutinated mass obtained and crushed is pulverized and then dissolved to separate the soluble compounds of beryllium, which are precipitated or dissolved in hydrofluoride acid and dried, giving beryllium oxyfluoride. This process gives off gases, among other fumes of hydrochloric acid (HF and dust.

(d) Pure beryllium is extracted from the oxyfluoride of beryllium in several ways. In the electrolytic method of Stock and Goldschmidt the salt is melted in a crucible, which liberates gaseous products and smoke.

In 1943, the United States Public Health Service reported (28) the results of an investigation "to measure and define the toxicity of beryllium and to indicate, as far as feasible by means of animal experiments, the maximum permissible concentration of dust or fumes from the metal or its compounds which workmen should be permitted to breathe."

Examination of the gases and fumes evolved during electrolysis of beryllium revealed that the fluoride content varied between 0.07 and 5.0 mg., and the beryllium content varied between 0.03 and 0.73 mg. per cubic foot. Sodium, beryllium, and barium fluorides were used. The fumes given off consisted of a true vapor phase and a very fine smoke or dust. Neither metallic beryllium nor beryllium oxyfluoride was found in the dust.

With a single exception, all guinea pigs were killed within 90 minutes or less when exposed to the dust and fumes. The toxic effect apparently was due to the fluoride dust and fumes, as the elimination of any one metal from the melt did not lessen the toxicity appreciably.

The Bureau of Industrial Hygiene of the Pennsylvania Department of Health in 1944 reported (29) the results of an investigation of the health hazards incident to manufacturing beryllium oxide in Pennsylvania and its use in the production of copper-beryllium alloys, which are employed in the manufacture of precision instruments, springs, and nonsparking tools.

A cursory examination of the medical records of the reported illnesses among plant workers in a month (September) selected at random indicated that 36 lost-time cases reported to the plant physician for treatment. Twenty-three of these (64 percent) were treated for dermatitis or a chest involvement and the remaining 13 (36 percent) were treated for injuries incurred through accidents. Of the illnesses treated, 14 were for dermatitis and 9 for chest involvement. Absenteeism was high - about 6 percent - and turnover averaged close to 100 percent a year.

The fact that employees exposed to fluorides in the plant still were reporting with respiratory diseases and dermatitis and that these diseases appeared more frequently than others indicated that fluorides probably were the cause. As fluorine plays an important role in the extraction of beryllium oxide from its ore, and the oxide retains a certain amount of soluble fluoride, the fluorine is present in many of the departments of the plant.

Thirty-seven atmospheric fluoride samples were collected and analyzed for fluorine, which, calculated as sodium fluoride, averaged 0.996 mg. per cubic meter of air.

In 1950 results were reported of a study of a "mysterious disease", which was first noticed in 1941 and was traced finally to exposure in manufacturing processes using beryllium or its compounds (30). Beryllium fluoride is mentioned as

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unquestionably being one of the salts causing the disease now known as pneumonitis. The fluoride process undoubtedly was responsible for the largest number of cases of pneumonitis and dermatitis among the workers observed in the study.

The following excerpt from the report (30) describes the steps in the processes and types of operation in each process in a plant manufacturing beryllium metal from raw beryl; the products are alloys of copper and beryllium from copper and beryllium oxide:

> The raw beryllium ore is first processed by grinding and heat treatment and then converted to the sulfate with sulfuric acid. Following a purification of the sulfate, the oxide is then produced from this salt in a calcining furnace. Treatment of the oxide with acid fluoride results in the formation of the beryllium ammonium fluoride, which is then reduced to beryllium fluoride by furnace treatment. Further furnace treatment of the beryllium fluoride results in the final product, beryllium metal. The beryllium copper alloys are produced by direct mixing of beryllium oxide with copper, in the presence of carbon and at required temperatures.
>
> The general types of operations involved in the plant process include grinding, treatment in tanks, crystallizing in centrifuges, furnace heating, and furnace product casting. Each of these processes is a potential producer of atmospheric contaminants in the form of dusts, fumes, or mists. The major potential hazards include beryllium dusts and fumes present as the ore, metal, oxide, copper alloy, and the various fluoride compounds, and acid mists and fumes of beryllium sulfate. Also present in the metal production process are dusts and fumes of other fluoride compounds and gaseous hydrogen fluoride.

Magnesium Foundries

The literature on the hazard of fluorine poisoning in magnesium foundries is meager. The following data are taken from reports of investigations in two magnesium foundries, one made in 1942 and the other in 1944.

Under pressure of the demands of the war industries, production of magnesium was greatly stimulated, and large-scale use of magnesium alloys resulted in an increase in the health hazards peculiar to this industry. Among these hazards is the use of any of a large group of soluble fluoride salts as inhibitors (31).

According to Williams (31), the chief exposures to fluorides in magnesium foundries are the shakeout, molding, melting, and core spraying. Sulfur, boric acid, and fluorides are used as oxidation inhibitors to treat sand in making sand molds in proportions ranging from 4 to 10 percent by weight, depending on physical factors in molding and casting. In core molding, core sands may be treated by mixing small quantities of sulfur and boric acid with the sand, or the finished cores may be sprayed with an aqueous (about 20 percent) solution of a fluoride, or both.

While melting magnesium by the crucible method (31), which is most commonly used, the metal is protected from oxidation by a fluoride-bearing flux. Flux is sprinkled on top during melting and is stirred in after all the metal is molten (about 65° C.). The charge is then heated to about 900° C. and removed from the furnace to a station where the dross is skimmed and a mixture of sulfur and borax (or some other inhibitor) is added. During this operation there is a brief but violent evolution of gases and fumes. The metal then is allowed to cool to pouring temperature of 700° to 800° C. Individual furnaces usually are ventilated to control sulfur dioxide fumes.

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Inhibitors in the sand are responsible for considerable air contamination during the shakeout. Fluorides in the sand are released, and high concentrations may be found in the air in the vicinity of the operation. This is usually the greatest single source of fluorides in a magnesium foundry, especially where there is a centralized shakeout. As the castings are broken out a mixture of steam, fluoride fume, magnesium oxide fume, dust, and various gases is given off. The amount of fluorides released during this operation depends on the size of the castings, concentration of the shakeout, amount of inhibitor in the sand, and the temperature of the castings when they are broken out. (F. C. Frary, Director of Aluminum Research Laboratories, Aluminum Co. of America, reported in a letter June 26, 1945, that some magnesium foundries use inhibitive sands that do not contain any fluorides.) The concentrations of fluorides found by Williams (31) at the various points of exposure are given in table 3.

TABLE 3. - Concentrations of fluorides in a magnesium foundry

	Shakeout	Molding	Melting	Core spraying
Number of samples	14	32	10	3
Range of concentrations found (mg. per 10 cu. m., expressed as fluoride	9.4-180	4.4-106	7.4-17.6	5.8-9.4
Average	87.7	18.8	12.6	7.0
Average deviation	+47.1	+14.5	+3.5	+2.0

In a study of the relationship between the urinary excretion and the bodily retention of fluorine, observations were made by Largent and Ferneau (32) in three magnesium foundries. In view of the report of Williams (31) that the greatest atmospheric contamination was in the shakeout area, Largent and Ferneau expected to find the highest urinary fluoride concentrations in samples provided by men working in that area. However, they found the highest concentration in samples from men in the core-spraying and pouring areas, although these areas have extensive ventilation. The cores are sprayed in spray booths and, in addition, the men are provided with respirators. As the atmosphere did not seem to be irritating, the workmen may not have worn their respirators consistently; the elevated fluoride concentrations in the urine possibly may have indicated laxness on their part.

Largent and Ferneau (32) concluded from their investigation that fluorine exposure is occurring in some foundry areas but not in others and that in some instances fluorine undoubtedly is being retained in the tissues but at a relatively low rate.

Bowler and coworkers (33) investigated the possibility of occurrence of fluorosis among workers in a foundry producing castings of magnesium-aluminum-zinc, magnesium-aluminum-manganese, and magnesium-aluminum-manganese-silver alloys. The following processes were carried out:

> The metal was melted in open crucibles or in an almost enclosed bale-out type of furnace; the flux used in every case contained a considerable amount of fluoride (about 15 percent); before pouring, the crust which formed on the melt was removed and a fluoride-containing dusting powder was sprinkled on top of the molten metal. Aluminum fluoride, to the extent of about 2 percent of the final mix, was added, either as solid or solution, to the sand used for moulding. Thus possible sources of danger from fluoride were as follows: (1) In adding the flux to the open crucibles; (2) in

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the application of dusting powder to the molten metal; (3) in sand preparation; (4) in casting and in the process of knocking out.

> The moulds were filled with sulphur dioxide from a cylinder immediately before pouring, a considerable amount being given off into the atmosphere, particularly during pouring. The high concentration of sulphur dioxide in the air was partly due to the fact that the dusting powder contained 60 percent sulphur.

The average raised level of fluorine excretion in the urine of workers examined and radiological evidence of bone changes in one of them suggests that at least some of the workers in the atmosphere of this magnesium foundry were exposed to a risk of fluorosis.

Petroleum Industry

The paraffin alkylation reaction (34), by which isoparaffin and olefin hydrocarbons interact to produce highly branched paraffinic motor fuels, was discovered by Ipatieff and Pines (35) more than a decade ago at the Research and Development Laboratories of the Universal Oil Products Co. (35). Since the discovery of this fundamental reaction, extensive laboratory and pilot-plant experimentation has been carried on to study the reaction with several catalysts. Investigations by Grosse and Linn (36) indicated that concentrated hydrogen fluoride was an excellent catalyst for alkylating isobutane with propylene, butylene, or amylenes. The olefins were completely converted in the presence of an excess of isoparaffin to give a saturated product, which has excellent antiknock properties and boils almost entirely in the aviation gasoline range.

According to Gerhold and his co-workers (34), although the catalytic properties of hydrogen fluoride were attractive, the commercialization of the process was delayed, largely because of the nature of hydrogen fluoride and the lack of experience in handling it in the manner and quantities required for hydrocarbon processing. When it became apparent that the facilities for producing aviation gasoline would have to be expanded to supply the war needs, the development of the hydrogen fluoride process was rapidly accelerated. Pilot-plant tests for investigating charging stocks, operating conditions, and materials of construction and process and mechanical designs of commercial plants that normally would have required years, were forced through in months.

Two major advantages of hydrogen fluoride alkylation over the older sulfuric acid process are the higher process temperature and the ease of catalyst regeneration. The higher temperature permits use of cooling water to remove the heat of reaction and thus eliminates critical refrigerating equipment. Catalyst regeneration is an inherent feature of the process; catalyst consumption is so low that the raw material and plant requirements for catalyst manufacture are considerably smaller than those for a sulfuric acid alkylation unit on the basis of equal alkylate production. Elimination of the problem of spent catalyst disposal, which is serious in many refineries using sulfuric acid alkylation, is a further advantage gained by fluoride catalyst regeneration.

Recently, a patent (U. S. patent 2,356,357) was granted to Schlesman and McCracken (37) for treating raw gasoline with boron trifluoride or hydrogen fluoride as catalysts. The raw gasoline, relatively high in olefin content, is treated with the catalysts mentioned at 300° to 500° F. and under 1,000 to 1,500 p.s.i. pressure, according to the claims. The treatment, it is asserted, reduces greatly the acid

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heat of the gasoline, a condition of primary importance, especially for aviation fuels. This means essentially that the olefin content of the fuel is reduced greatly, either by saturation or by polymerization to heavier products, which may be eliminated from the final product by distillation. Little has been published about the use of boron fluoride as a catalyst, although it has been studied extensively in research laboratories and is said to show some unusual results. Boron trifluoride, BF_3, is a gas at ordinary temperatures, boiling at -101° C., (-149.8° F.), whereas hydrogen fluoride, HF, boils at 67° F., or about room temperature.

The first commercial hydrogen fluoride plant was put in operation in December 1942, and several more were built during 1943 (38). When used as a catalyst, hydrogen fluoride may be a poisoning hazard unless it is confined within the processing equipment; therefore, new measures had to be adopted and rigidly enforced to protect the personnel of plants employing hydrogen fluoride (39). The principal sources of poisoning are from accidental spills of acid in the plant area owing to failure to evacuate properly; failure of the seals on pumps, contactors, or valves; or rupture of lines or vessels. There is also the possibility of accidental discharge of acid, which may injure those exposed to it. Burns may result from handling tools that may have been in contact with the acid. There is a possibility of pump and packing failures when adjustments are made to operating conditions. Repairmen may be exposed to high concentrations of hydrogen fluoride while repairing an extremely large leak.

Benson (39) states that it is almost impossible for anyone consciously to inhale enough hydrogen fluoride to harm himself seriously; the acid gas is too pungent for voluntary inhalation. Unconsciousness and injury will result only if a man is trapped when gases are released suddenly.

Other Industries

There are other industries and occupations in which a possible fluorine-poisoning hazard exists, such as the electrochemical process (40) for the production of fluorocarbons, in which the escaping gas carries with it a certain amount of hydrogen fluoride and volatile fluorocarbon products that may be produced; welding; pickling metals; manufacturing hydrofluoric acid and fertilizers; and many other occupations not mentioned because few people are so employed.

In a study of welding fumes with stainless-steel electrodes, Drinker and Nelson (41) found that the fumes contained 17.6 percent fluorine and that, theoretically, hydrogen fluoride could be evolved from the coating of the rods. However, they burned a great many such electrodes in response to complaints about the irritating nature of the fumes without finding hydrogen fluoride, although fluoride compounds were present. According to Ready (42), fumes from these rods may carry silicon fluoride, which, when inhaled, breaks down into hydrofluoric acid and silicon dioxide, and continued breathing of even slight concentrations of fumes from these special arc welding rods may cause fluoride poisoning.

Pickling baths containing 2 to 5 percent hydrofluoric acid in solution or barium fluoride in suspension are used extensively in the sheet-metal industry to remove coatings of scale. This process is particularly adapted to cleaning aluminum or dural parts of airplanes before they are painted (42). Fluorine vapors from the vats may be a source of poisoning if measures are not taken to prevent their inhalation by employees.

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In 1938, Wolff and Kerr (43) reported a case of chronic fluorine poisoning in a worker who had been exposed almost daily for 18 years to finely ground rock phosphate dust containing 3.88 percent fluorine.

It is interesting to note that a cement company (44) recently has adapted a process for manufacturing superphosphate to defluorinating raw rock phosphate, which is materially helpful in meeting a critical shortage in the bone meal necessary to the expanded livestock-raising program. The present supply of animal bone, most of which used to be imported from South America, falls far short of the demand, and much experimenting has been done to process rock phosphate for use as a substitute. Raw rock phosphate cannot be used for this purpose as it contains too much fluorine, which is toxic to animals when present in large enough quantity. The Florida pebble phosphate used contains 3.76 percent fluorine, whereas the defluorinated product is guaranteed to contain a maximum of 0.3 percent and actually contains 0.08 to 0.12 percent (44). The pebble phosphate is pulverized and mixed with sulfuric acid. The reaction produces heat, steam, and dust. The operation is enclosed as tightly as possible, and an exhaust fan carries the dust and fumes to a wood stack, where water sprays bring them down in solution or suspension. The liquid contains about half of the fluorine and probably some sulfuric acid. It would appear that unless care is taken to completely protect the employees from the dust and fumes, a fluoride-poisoning hazard may exist during the defluorinating process.

According to the Oil, Paint, and Drug Reporter (45), six different plants are producing defluorinated phosphate rock on a permanent basis by processes developed in cooperation with the Agricultural Research Administration. These processes have been used by manufacturers in preparing nearly 100,000 tons of feed phosphate virtually free of fluorine.

Numerous cases of accidental poisoning by ingestion of insecticides containing fluorine are recorded in the literature, but apparently no information is available regarding poisoning of persons eating fruit and vegetables that have been sprayed by liquids containing fluorine compounds. However, the Food and Drug Administration (46) proposed in 1944 to limit the fluorine content of insecticide residue on apples and pears to 7 mg. of fluorine, calculated as F, per kilogram of apples or pears (45). The grounds for this proposed regulation were that fluorine and many of its compounds are poisonous and deleterious substances and, therefore, the quantity of insecticidal residue remaining on the fruit should be as small as practicable.

Fluorine compounds were used in connection with the production of the atom bomb. A report of research work done under the Manhattan Project and the Atomic Energy Commission on the pharmacology and toxicology of uranium compounds, including a section on fluorine and hydrogen fluoride, was published in 1949 (47). Details of the use of the fluorine compounds are not given. The statement is made, however, that fluorine found wide application in the chemical technology associated with the production of uranium. Never before had such quantities of elemental fluorine gas been handled daily. The handling of large volumes of hazardous gas under pressure made the danger of sudden release of large quantities a real one, and continuous exposure to low concentrations from unavoidable losses from the equipment was a source of considerable concern.

TOXICITY OF FLUORINE COMPOUNDS

More space than is available here would be required to discuss in detail the properties of all the toxic fluorine compounds and the health hazards incident to exposure thereto. Therefore the physical and toxic properties of some of the compounds are summarized in table 4.

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TABLE 4. - Physical and toxic properties of fluorine compounds (Con.)

Compound	Formula	Description	Derivation	M. Wt.	Sp.gr. or density	B.P., °C.	M.P., °C.	Uses	Handling and storage	Physiological action	M.A.C.
Ammonium bifluoride	$(NH_4)FHF$	White crystals	Action of NH_4OH on HF with subsequent crystallization.	57.05	1.211	-	Sublimes	Ceramics; chemical reagent; etching glass; sterilizer for brewery, dairy, and other equipment.	Personnel exposed to dust should wear respiratory equipment and chemical safety goggles, and avoid skin contact.	Very irritating to skin, eyes, and mucous membranes.	-
Ammonium fluoride	NH_4F	do.	do.	37.04	1.315	-	do.	Fluorides, anal.chem. in agriculture, antiseptic in brewing, etching glass, textile mordant.	do.	Toxic.	-
Ammonium silicofluoride	$(NH_4)_2SiF_6$	White crystalline powder	-	-	2.01	-	Soluble in alcohol and water	Medicine (antiseptic).	-	-	-
Antimony pentafluoride	SbF_5	Oily liquid	Direct union of Sb and F_2.	216.76	2.990	149.5	70	Ceramics, mordanting cotton.	Store in cool, ventilated place away from areas of acute fire hazard.	Will fume in moist air and evolve HF, which is very toxic.	-
Antimony trifluoride	SbF_3	Octrahedral crystals	do.	178.8	4.379	Sublimes	292	Ceramics, mordanting cotton.	-	Caustic and toxic material.	-
Barium fluoride	BaF_2	White powder	Interaction of BaS and HF	175.36	4.83	2,137	1,280	Enamels, antiseptic, enbalming fluids.	-	Toxic.	-
Barium silicofluoride (barium fluosilicate)	$BaSiF_6$	White crystalline powder	-	279.42	4.21	-	Slightly soluble in water	Ceramics, insecticide, insecticidal compositions	Solid material is dangerous to eyes, which should be protected.	do.	-
Beryllium fluoride	BeF_2	Amorphous colorless	-	47.02	1.986	-	800	-	-	One of the most toxic of beryllium compounds. Can cause lachrymation and catarrhal conjunctivitis. Has an irritant action on skin, mucous membranes, and conjunctiva, although this aspect is rarely serious. May cause pneumonitis.	2 micrograms per cu. meter in working area; 0.01 micrograms of Be per cu. meter in a nonworking area.
Beryllium potassium fluoride (glucinum potassium fluoride)	$BeF_2(KF)_2$ $GlF_2(KF)_2$	White crystal masses	-	163.30	-	-	-	-	-	Toxic.	-
Beryllium sodium fluoride (glucinum sodium fluoride)	$BeF_2(NaF)_2$ $GlF_2(NaF)_2$	do.	-	131.10	-	-	-	-	-	do.	-
Boron trifluoride	BF_3	Colorless gas	-	67.82	2.99	-101	-127	-	Nonflammable gas. Should be used in closed system if possible.	do.	-
Calcium fluoride	CaF_2	Cubic, colorless crystals	Occurs in nature as fluorite or fluorspar.	78.08	3.180	1,360	-	Flux in metallurgy; manufacture of HF; ceramics; enamels, etching glass; calcium cyanamide.	-	do.	1 to 2.5 mg. per cu. meter.
Carbonyl fluoride (fluoroformyl fluoride)	COF_2	Colorless gas	Action of silver fluoride on CO.	66.01	1.139	-83	-114	-	-	do.	-
Chlorine trifluoride	ClF_3	Corrosive liquid, colorless gas	-	92.46	1.77	11.3	-83	-	-	-	-

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TABLE 4. - Physical and toxic properties of fluorine compounds (Con.)

Compound	Formula	Description	Derivation	M. Wt.	Sp.gr. or density	B.P., °C.	M.P., °C.	Uses	Handling and storage	Physiological action	M.A.C.
1-chloro-1, 1-difluoroethane	$ClF_2C_2H_3$	-	-	100.50	-	-	-	-	Personnel should wear protective clothing for prolonged exposure or high concentration and where necessary chemical safety goggles and respirators.	Slightly toxic.	128,000 p.p.m. for 4 hr. exposure killed 3 of 5 white mice. 14 days observation.
Copper fluoride	$CuF_2 2H_2O$	Monoclinic blue crystals	Decomposition of copper carbonate with HF	137.60	2.93	-	Soluble in water, alcohol, and acids	Ceramics, enamels.	-	Toxic	-
Cryolite	Na_3AlF_6. or $3NaF.AlF_5$	Monoclinic colorless crystals	Treating soluble soda and alumina salts with HF.	209.96	2.90	-	1,000	Glass, enamels, aluminum manufacture (flux), insecticides.	Exposed personnel should wear protective equipment and respirators in high concentrations.	Can cause irritation of skin and respiratory passages and changes in bone structure that may be disabling.	A daily intake of 28 mg. for many years believed required to cause osteosclerosis.
Cyanogen fluoride	CNF	Colorless gas	Interaction of silver fluoride and cyanogen iodide.	45.02	2.335	-	Sublimes	Organic synthesis; military poison gas (lachrymator).	-	Liquid and vapor dangerous to eyes.	10 p.p.m.
1,1-dichloro-2, difluoroethylene	-	-	-	-	-	-	-	-	-	Moderately toxic.	1,000 parts 4 hrs. a day for 14 days killed an average of 3 of 6 white mice.
Dichloro-difluoromethane	CCl_2F_2	Colorless gas.	Freon-12.	120.92	-	-29	Insoluble in water	Refrigerant.	Should be used with moderately good ventilation. Noncombustible and nonexplosive.	In contact with hot surfaces can decompose into toxic compounds, such as chlorine, hydrogen chloride, fluorine, hydrogen fluoride, or phosgene.	2,000 p.p.m.
Dichloro-monofluoromethane	$ChCl_2F$	Colorless gas, faint ether-like odor.	Freon-21.	102.93	89°C.	-127	-	do.	-	More harmful than difluoromonochloromethane and more potent than trichloromonofluoromethane.	1,000 p.p.m.
Dichlorotetrafluoroethane	CCl_2FCF_3	Colorless gas.	Freon-114	171	-	3.5	-	do.	-	Same decomposition as above in contact with hot surfaces.	-
Diethylfluorophosphate	$(C_2H_5O)_2POF$	Liquid with sweet or fruity odor.	-	156.10	1.15	170	Low	-	Should be used in closed system. Do not use near hot surface or open flame. Personnel exposed should wear chemical safety goggles to protect eyes.	Can cause narcosis. Somewhat more toxic than chlorofluoro derivatives. Same decomposition products as above. Irritating to eyes. Has been known to cause miosis.	0.50 mg./liter 10 minutes exposure for 10 days lethal for 50 percent of mice exposed.
Difluoroethane	Ch_3CHF_2	Colorless liquid gas.	-	66.05	1.004	-24.7	-117.0	-	Should be used and stored with adequate ventilation.	Slightly toxic.	64,000 p.p.m. 4 hrs. daily for 14 days killed 3 of 6 white mice.
1,1-Difluoroethylene	$CH_2:CF_2$	Colorless gas.	-	64.04	-	Below -70	-	-	-	do.	128,000 p.p.m. 4 hrs. daily for 14 days killed 3 of 6 white mice.
Difluoromonochloromethane	$CHClF_2$	-	Freon-22.	86.48	-	-41	-	Refrigerant.	-	Can cause mild narcosis. Of low toxicity.	2,000 p.p.m.

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TABLE 4. - Physical and toxic properties of fluorine compounds (Con.)

Compound	Formula	Description	Derivation	M. Wt.	Sp.gr. or density	B.P., °C.	M.P., °C.	Uses	Handling and storage	Physiological action	M.A.C.
Difluorophosphoric acid anhydrous	-	Corrosive liquid	-	-	-	-	-	-	Avoid contact or inhaling Wear protective devices, goggles, rubber gloves, and rubber aprons.	Can react with metals to evolve hydrogen gas. Can cause caustic burns of eyes, skin, and mucous membranes. Is an irritant.	-
Diisopropylfluorophosphate	$(C_3H_7)_2POF$	Oily liquid.	-	152.19	1.07 (approx.)	183	Above	Potent tool in investigation of mechanism of transmission of nerve impulses (25).	Those exposed should wear protective equipment.	Can damage eyes; is generally regarded as an irritant. According to Larner (25) it is extremely toxic; causes such nervous symptoms as pupillary narrowing, sweating, lachrymation, salivation, and diarrhea.	0.60 mg./liter for 50 percent of mice for 10 minute exposures for 10 days.
Dimethylfluorophosphate	$(CH_3O)_2POF$	Liquid	-	128.05	1.28 (approx.)	-149	Low	-	Exposed personnel should wear protective equipment including chemical safety goggles.	-	0.29 mg./liter for 50 percent of mice exposed for 10 minutes per day for 10 days.
Disulfur decafluoride	S_2F_{10}	Colorless mobile liquid.	One of the products formed in commercial production of SF_6.	-	2.08 gm per ml at 0°C.	29	-	-	Decomposes in contact with body tissues to yield some hydrogen fluoride.	Acts as a primary pulmonary irritant and is 3 times as toxic as phosgene to mice and dogs.	1 p.p.m. kills rats after exposure of 16 to 18 hrs.
Ethyl fluoride or fluoroethane	CH_3CH_2F	Colorless gas.	-	48.06	0.8158 at -37.7°C.	-37.7	-143.2	-	-	Only slightly toxic.	256,000 p.p.m. killed 3 of 6 white mice 4 hrs. daily exposure for 14 days.
Ethyl fluoroformate	C_2H_5COOF	Liquid	Interaction of ethylchloroformate and thallium fluoride.	92.07	1.11 at 33°C.	57	-	Military poison gas (lachrymator).	-	Very irritating.	-
Ethyl fluorosulfonate	-	do.	-	-	-	-	-	do.	-	do.	-
Fluoboric acid	-	do.	-	-	-	-	-	-	Store in wax or lead containers away from fire hazard. Exposed personnel should wear protective clothing, gastight chemical goggles, and respirators.	A powerful caustic and very corrosive liquid. Can cause serious burns. Mists and vapors extremely irritating to upper respiratory tract and lungs.	-
Fluorine	F_2	Green-yellow gas.	By electrical deO composition of anhydrous hydrofluoric acid at -23°C.	38.00	1.69 at 15°C.	-187	-223	Organic synthesis; fluorine compounds.	Must be handled with great care. Exposed personnel should wear protective clothing.	Very caustic and corrosive. Prolonged absorption causes bone changes.	1 mg./cu. meter to 3 mg./cu. meter
Fluoroacetic acid	CH_2FCOOH	Colorless crystals.	-	78.04	-	165	33	As rodenticide called "1080" (25).	Avoid inhalation of vapors, fumes, and dust. Protective clothing should be worn; also goggles and respirators.	Toxic and corrosive.	1 mg./kg.lethal for hogs, 14 mg./kg. lethal for chickens (25).
Fluoroacetphenone or phenacyl fluoride	$C_6H_5COCH_2F$	Brown liquid.	By Friedlcraft synthesis.	-	-	-	98 at 8 min.	Suggested military gas.	Avoid inhaling the vapors; wear protective clothing and goggles.	Irritant.	-
Fluoroform or Trifluoromethane	CHF_3	Colorless gas.	-	70.02	-	-82.2	-163	-	When exposed to high temperatures or open flames can decompose into other extremely toxic products.	Can cause wild narcosis, effects usually of short duration. Can be substituted for N in air and guinea pigs can exist in such atmosphere without apparent harmful effects.	Extremely low toxicity.

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TABLE 4. - Physical and toxic properties of fluorine compounds (Con.)

Compound	Formula	Description	Derivation	M. Wt.	Sp.gr. or density	B.P., °C.	M.P., °C.	Uses	Handling and storage	Physiological action	M.A.C.
O-fluoro-benzoic acid	FC_6H_4COOH	-	-	140.11	1.460	-	122	-	-	-	700 mg./kg. (26).
Fluosilicic acid; or silicofluoric acid; or hydrofluosilicic acid.	H_2SiF_6	Transparent, colorless, fuming liquid.	-	144.08	1.29-.31	-	-	Insecticide.	Keep away from acute fire hazards, with containers tightly closed.	Very toxic, irritant, and corrosive. Can cause burns on skin and mucous membranes.	33 mg./cu. meter inhaled for 6 hrs. caused death in guinea pigs.
Fluosulfonic acid or fluosulfuric acid	HSO_3F	Colorless liquid.	-	100.07	-	163	Soluble in water.	-	Fuming, highly corrosive liquid.	Corrosive and toxic.	-
Fluorotyrosine	-	-	-	199	-	-	-	-	-	Is an exception to the general rule that organic fluorine compounds are less toxic than inorganic (25).	11 mg./kg. lethal dose for mouse (25).
Formyl fluoride	HCOF	Colorless mobile liquid.	-	48.02	-	-26	Soluble in water.	-	Decomposes slowly to form hydrofluoric acid and carbon monoxide.	Three times more toxic than chloropicrin.	-
Heptafluoro-butyric acid	$CF_3CF_2CF_2COOH$	Colorless liquid.	-	214	-	120 at 735 mm.	-	-	Very hygroscopic. Handle with caution.	A strong toxic and corrosive acid.	-
Hexafluorophosphoric acid	-	Corrosive liquid				-	-	-	See fluorides and phosphoric acid.	Toxic and corrosive liquid.	-
Hydrofluoric acid; or hydrogen fluoride; or fluorhydric acid	HF	do.	Powdered CaF_2 treated with H_2SO_4 and mixture distilled. HF_2/gas passes over and is dissolved in distilled water.	20.01	0.921 (g) gm./liter (l) 0.987	-	-	Chemicals, analytical reagent; etching glass; ceramics and numerous other industries.	Good safety equipment should be at hand, protective clothing, including gloves and rubber shoes or boots, should be stored in lead carboys.	Toxic, corrosive. Vapor or liquid is very dangerous to eyes, skin, or any part of body. Burns may not become noticeable for some hours. Not considered a source of chronic poisoning. Large amounts in the eye cause immediate blindness.	3 p.p.m. (Conf. Govt. Ind. Hyg.) 50 p.p.m. or more considered fatal in 30 to 60 minutes.
Lithium fluoride	LiF	Fine white powder.	Action of HF_2 on LiOH.	25.94	2.601	1,676	870	In enamels.	-	Toxic.	-
Manganic fluoride	MnF_3	Red crystals.	-	11.93	3.54	-	Decomposed by heat and water.	-	Store away from acute fire hazards and from sprinkling systems or other sources of moisture.	Toxic material.	-
Mercuric fluoride	HgF_2	Transparent crystals.	-	238.61	8.95 at 15°C.	650	645	-	Shipping regulations require Poison B label.	do.	-
Methyl fluoroformate	CH_3COOF	-	-	78.04	1.06 at 33°C.	40	-	Has been used as a military poison of lachrymatory type.	Particular attention should be paid to eyes. Respirators, goggles, and protective clothing should be worn by those exposed.	Very irritating.	-
Methylfluoro-sulfonate	CH_3OSO_2F	Liquid	-	114.09	1.427 at 16°C.	92	-	Used as a military poison gas of the toxicant variety.	Very corrosive material that attacks glass. Exposed persons should wear gastight chemical safety goggles, a full face shield, respirators, and protective clothing.	Very corrosive and highly toxic.	-
Monochlorotetrafluoroethane	C_2HF_4Cl	Nonflammable gas.	-	136.49	-	-	-	-	Do not use near hot surfaces or open flame; heat can decompose into very toxic products. Prohibits smoking near where material is in use.	If released in large quantity may lower concentration of oxygen below point necessary to support life.	-

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TABLE 4. - Physical and toxic properties of fluorine compounds (Con.)

Compound	Formula	Description	Derivation	M. Wt.	Sp.gr. or density	B.P., °C.	M.P., °C.	Uses	Handling and storage	Physiological action	M.A.C.
Monochlorotrifluoromethane or chlorotrifluoromethane	$CClF_3$	Colorless gas.	-	104.47	-	-80	-181	-	See monochlorotetrafluoroethane.	Asphyxiant.	-
Monofluorophosphoric acid	H_2PO_4F	Corrosive liquid	-	116.03	-	-	-	-	Corrosive.	-	-
Monofluorotrichloromethane F11	CCl_3F	Colorless liquid	-	137.38	1.494 at 17.2°C.	24.1	-111	Refrigerant.	At high temperatures can decompose to form toxic products, such as HF,HCl, and possibly phosgene. Personnel should be cautioned against smoking while working with this material.	Only slightly toxic. Will cause irritating symptoms, cramps, and paralysis. Gives warning by irritation of eyes and respiratory passages.	1,000 p.p.m. Between 45,000 and 51,000 p.p.m. caused marked loss of coordination in guinea pigs exposed for 2 hours.
Potassium aluminum fluoride	K_3AlF_6	White powder.	-	-	-	-	-	-	-	Toxic material.	-
Potassium beryllium fluoride	$BeF_2 2KF$	White crystalline mass.	-	173.2	-	-	Soluble in water.	-	-	Toxic.	-
Potassium bifluoride; French salt; potassium fluoride, acid	KHF_2	Colorless crystals.	-	78.10	-	-	Decomposes	-	-	Very toxic and corrosive.	-
Potassium fluoride	KF	White, crystalline deliquescent powder.	-	58.10	2.48	1,500	880	-	-	Toxic.	-
Propylene fluorohydrin	-	-	-	-	-	-	-	-	Personnel exposed should be cautious. Respirator recommended to avoid excessive inhalation.	Moderately hazardous.	4,000 p.p.m. for 4 hours day for 14 days killed 3 of 6 white mice.
Silicon fluoride; or silicon tetrafluoride	SiF_4	Colorless gas	-	104.06	4.67 gm./liter	-65 at 181 mm.	-77	Manufacture of fluosilic acid, chemical analysis.	Hydrolizes in presence of moisture to evolve hydrogen fluoride, which is very toxic.	Toxic.	-
Silver fluoride	$AgF.H_2O$	Yellow crystalline mass.	-	144.9	5.852	-	435	-	-	do.	-
Sodium fluoride; or villiaumite	NaF	Clear, lustrous crystals.	-	42.00	2.558	1,700	980-997	-	-	Toxic.	-
Sodium fluosilicate	Na_2SiF_6	White powder.	-	188.1	2.7	-	-	-	-	do.	-
Stannous fluoride; or tin bifluoride, tin fluoride	SnF_2	do.	-	156.70	-	-	-	-	-	do.	-
Sulfur hexafluoride	SF_6	Colorless gas.	-	146.06	6.50 gm./liter	-63.8 sublimes	-56	-	Chemically inert and believed to be physiologically inert in the pure state. Personnel should be protected against possible exposure to HF.	Can contain variable quantities of lower sulfur fluoride, some of which are toxic very reactive chemically, and corrosive in nature. Hydrolizes in contact with water to yield HF, which is highly toxic and very corrosive.	-
Sulfur monofluoride	S_2F_2	do.	-	102.12	Liq. 1.5 at -100°C.	-99	-105.5	-	Store in cool place away from moisture.	Is hydrolized by water to HF, which is highly toxic.	-
Sulfur tetrafluoride	SF_4	Gas.	-	108.06	-2.75	-44.8	16.83	-	Exposed personnel should wear protective clothing.	Chemically reactive, corrosive, and toxic.	-

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TABLE 4. - Physical and toxic properties of fluorine compounds (Con.)

Compound	Formula	Description	Derivation	M. Wt.	Sp.gr. or density	B.P., °C.	M.P., °C.	Uses	Handling and Storage	Physiological action	M.A.C.
Tetrafluoroethylene, inhibited; or perfluoroethylene	$CF_2:CF_2$	Colorless gas.	-	100.02	-	-78.4	-142.5	-	Nonflammable. Should be stored carefully to avoid mechanical injury to containers.	A high enough concentration can cause asphyxiation.	-
Trifluoroactic acid	CF_3COOH	Colorless liquid.	-	114	-	71.1 at 734 mm.	-	-	Strong acid comparable to hydrogen chloride. Personnel should avoid inhaling fumes and repeated skin contact.	Corrosive and irritating to skin, eyes, and mucous membranes. Very dangerous to the eyes.	-
Trifluorochloroethylene; or monochlorotrifluoroethylene	C_2F_3Cl	Colorless gas.	-	116.48	-	-27.9	-157.5	-	Nonflammable. Should be stored carefully to avoid mechanical injury to containers. Store in ventilated area out of direct rays of sun.	Can cause asphyxiation by reducing oxygen content of air, if it escapes in enclosed area.	
*Uranium hexafluoride	UF_6	Volatile compound	Prepared by action of fluorine on uranium, pentachloride; treating uranium or uranium carbide with fluorine in the presence of chlorine.	-	-	56.4	-	Fluorinating agent.	Extremely corrosive. Readily hydrolyzed by water, forming uranyl fluoride. Extremely reactive toward most substances.	According to mortality the susceptibility of (1) mouse and rabbit is high; (2) rat, medium; and (3) guinea pig and dog low.	20 mg./cu. meter killed 100 percent of mice and rabbits and 40 percent of dogs. 3 mg. level was lethal only to the mouse and rabbit. A 7-fold decrease in concentration 0 UF_6 in air from 20 to 3 mg. reduced the mortality in rats from 75 to 0 percent, in guinea pigs from 45 to 5 percent, and in dogs from 40 to 20 percent. Mortality of mouse and rabbit changed only from 100 to 92 percent by same decrease, owing to high susceptibility.
*Uranium tetrafluoride	UF_4	Green powder.	Prepared in dry way and wet way by reactions employing HF	-	6.	-	960-965	Fluorinating agent widely used in uranium chemical industries.	Toxicity studies were made with dust, which is nonlaygroscopic. Dust moderately soluble in water.	Mortality most pronounced in cat and dog, less in rat, rabbit, and guinea pig. Clinical signs of poisoning: anuria, polydipsia, rhinitis, conjunctivitis, vomiting, and muscular weakness.	40 mg./cu. meter lethal to 21 percent of 66 animals first 9 days of exposure. Mortality from exposure noticeable only at a range of approximately 18 to 40 mg./cu. meter (27).

*Data on uranium fluoride compounds obtained from report of experimental studies by the Division of Pharmacology of the Manhattan Department of the University of Rochester. (See ref. 27).

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Most of the data in the table, especially those on physiological effects, are taken from Handbook of Dangerous Materials by Sax (48). Some material on uses and constants is quoted from the Condensed Chemical Dictionary (9). A few of the most toxic compounds are discussed in detail following the table.

From a practical toxicological point of view the fluorine compounds may be divided into four groups (27):

1. Gaseous fluorine compounds, partly the very toxic hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4), partly a number of less toxic organic compounds such as dichlorodifluoromethane (CCl_2F_2), dichlorotetrafluoroethane, ($C_2Cl_2F_4$), and others.

2. Solutions of hydrofluoric acid (HF) and hydrofluosilic acid (H_2SiF_6), which are extremely toxic. This group includes acid solutions of fluorides, silicofluorides, and bifluorides in substance.

3. Fluorides and fluosilicates relatively easy to dissolve, which have a high degree of toxicity: Sodium fluoride (NaF), potassium fluoride (KF), ammonium fluoride (NH_4F), sodium fluosilicate (Na_2SiF_6), potassium fluosilicate (K_2SiF_6), and ammonium silicofluoride ($(NH_4)_2SiF_6$). A fluoride has the same toxicity as the corresponding fluosilicate, if its content of fluorine is taken into account.

4. Almost insoluble fluorine compounds, the toxicity of which is moderate or low: Cryolite (Na_3AlF_6), calcium fluoride (CaF_2).

History of Poisoning by Fluorine Compounds

The Nuremberg artist Schwanhard (1670) is credited with the first attempts to etch glass using the vapors that are generated when fluorspar is treated with sulfuric acid. In 1771, Scheele produced the aqueous solution of hydrogen fluoride. In 1803, an Italian chemist, Dominico Morichini, demonstrated the presence of fluorine in a fossil elephant tooth found outside of Rome. In 1809, Gay-Lussac and Thenard described the corrosive effect of the acid upon the skin and showed that fluorine is present also in fresh teeth of animals and man. About 1846, George Wilson, the Scottish chemist, determined that fluorine is widespread in nature in springs and sea water, vegetable ash, and blood and milk of animals (49).

It is only within comparatively recent years that the serious nature of fluoride toxicity has been realized, particularly as to chronic effects (50). It is from this viewpoint that the industrial use of fluorine is important. The possibility of a health hazard from fluorine compounds should be recognized wherever they are employed in industry or discharged into the air as waste gas.

Fluoride poisoning of human beings, animals, and vegetation by waste gases discharged from smelters, where the element is present in the ore or is used as a flux in roasting metals, has been a possible, although often unrecognized, hazard for many years. At one time the very existence of the smelter industry in Great Britain and Germany is said (51) to have been threatened by the many burdensome laws and regulations enacted to force the adoption of measures to prevent discharge into the atmosphere of harmful gases. In 1907, Ost (51) stated that an animal disease, consisting of diarrhea, anemia, and atrophy of the bones, which existed in the neighborhood for 20 years, brought the greatest danger to the Freiberg (Germany) smelters. In 1855, the Freiberg smelters had to pay the first damages to the injured inhabitants. These damages reached the maximum of 61,000 marks in

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1864, and in 1870, 18,000 marks were paid. Later, the damages amounted to 3,000 to 4,000 marks a year, until, in 1893 a total of 880,000 marks has been paid for current injuries and 644,000 for permanent relief (51).

Many of the cases of poisoning mentioned in the literature have resulted from oral ingestion of fluorine compounds, although poisoning from inhaling fluoride dust and hydrofluoric vapor has occurred. German workers in an electrolytic plant manufacturing beryllium exposed to dust of sodium silicofluoride and sodium beryllium-fluoride as well as to active gaseous fluorine compounds (HF, SiF_4) developed symptoms of fluoride poisoning (49). Frostad (49) described fluoride intoxication among the workers at a long-established Norwegian aluminum works. Investigators handling fluorine compounds have suffered from protracted diseases of the air passages, and the Belgian chemist Louyet died when he was 32 years old of a pulmonary affection probably owing to exposure to such compounds (49). Roholm (49) found in the literature mention of only two cases of acute poisoning from inhaling gaseous fluorine compounds. Both were workers in a superphosphate factory in Dublin and were reported by Cameron (52) in a publication in 1887.

During the years 1911-1918, a disease like osteomalacia (softening of the bones) appeared in the vicinity of aluminum works in Switzerland, the etiology of which was not clear. After long litigation, the works had to compensate for smoke damages to vegetation but were declared not liable for the cattle disease, as expert witnesses considered the affection to be an ordinary osteomalacia (49). However, Cristiani, who had been called in as an expert when the disease had almost disappeared, and Gautier (49) expressed the hypothesis that the affection was chronic fluoride poisoning produced by an abnormally high fluorine content of the vegetation close to the works, as a result of the emanation of gaseous fluorine compounds (HF, H_2SiF_4). The disease occurred within a distance of 4 to 5 kilometers of the works. Cristiani and his collaborators (49) were able experimentally to produce chronic fatal poisoning in guinea pigs by means of ingested fluorine compounds and to obtain the same picture by feeding fodder reaped near the factory on the windward side and fodder that had been exposed experimentally to hydrofluoric vapor. The cattle disease sometimes ended in death in the course of months. About one-third of 450 cattle were attacked.

In 1912, Bartolucci (49) described a strange disease among cattle on a farm close to a superphosphate factory in Italy. The cattle became thin and the coat coarse and lifeless; the animals lay down and got up with difficulty, limped, and stood with curved, stiff backs and stiff hindquarters. Tender swellings appeared at the joints and, after 4 or 5 months, there was thickening of the ribs and bones of the head and shoulders. Finally, a cachectic condition (general ill health and malnutrition) developed, and the cattle had to be slaughtered. Bartolucci (49) described the disease as osteitis, conforming clinically to classical osteomalcia, and associated it etiologically with the content of fluorine compounds in the waste gases from the works.

Probably the most spectacular instance of the ill effects of fumes discharged from factories was the fog disaster in the Meuse Valley in Belgium. At the beginning of December 1930, a thick mist lay over large parts of Belgium, and several thousand cases of acute pulmonary attacks, with 60 deaths, occurred from December 3 to 5 in the densely populated valley east of Liege. A Belgian investigating commission concluded that the deaths were caused by poisonous products in the waste gases. Although it was impossible to indicate any definite substance, the commission was of the opinion that the offender was sulfur dioxide or its oxidation products, quantities of which were found in the factory smoke.

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In 1931, Storm van Leeuwen of Leiden (53) advanced the theory that the cause of the Meuse Valley disaster was gaseous fluorine compounds emanating from certain smelters in the region that were treating zinc ores containing fluorine. Fenner (54), who had followed the matter with great interest, assumed that HF, and especially SiF_4, could play a part, and the publication of van Leeuwen's article strengthened his opinion, as the symptoms observed were similar to those of hydrofluoric acid poisoning. According to Fenner (54), the fluorine escaped for the most part as SiF_4 and not as HF. SiF_4 is especially decomposable in water, but not quantitatively, and undecomposed silicon fluoride can be present in the atmosphere. He mentioned, also, that H_2SiF_6 and the still less known silicon fluorhydrine might have been present. Fenner remarked that if hydrofluoric acid has a toxic as well as an irritating action, in this instance it appeared to be a question of compounds whose acid action was considerably slower than their toxic.

In a discussion in 1937 of the cause of the Meuse Valley disaster, Roholm (55) refers to the lack of knowledge of the toxicity of fluorine compounds at that time and reviews some of the important literature that has appeared since 1930 in confirmation of the opinion that the Belgian disaster was due to fluorine compounds. In this review, Roholm (55) stated that the presence of gaseous fluorine compounds in the area affected was beyond question. Fifteen of the 27 factories in the area handled raw materials containing fluorine or added fluorine compounds to the raw materials and, consequently, were capable of discharging gaseous fluorine compounds from their smoke stacks. The 15 industries mentioned comprised 4 very large iron works with blast furnaces and steel works, 3 large metal works, 4 glass works and ceramic factories, 3 zinc works, and 1 superphosphate factory.

A number of parallels can be cited between the occurrence of the toxic fog in the Meuse Valley of Belgium and that of Donora, Pa., on October 27-29, 1948.

1. Both incidents occurred in industrialized valleys.

2. Industries in both areas included blast-furnaces, steel plants, zinc plants, and glass and ceramic plants.

3. Unusually dense fogs, with little or no air movement and high barometer, existed for several days.

4. The symptoms of affected persons were similar.

5. Elderly persons, or those with respiratory or heart conditions, were most severely affected.

6. In both instances deaths began to occur on the fourth day of fog. Nineteen deaths occurred in 36 hours in the Donora smog, and several hundred people in the area were affected in varying degree.

According to the Journal of the American Medical Association (54) the disaster at Donora was a problem of air pollution by industrial gases and fumes containing sulfur dioxide, arsenic, and fluorine, originating from smelters.

In the opinion of Sadtler (57), consulting chemist employed by the Borough of Donora, the deaths were due to fluorine not sulfur dioxide.

A complete study by the United States Public Health Service (58) of all the conditions surrounding the Donora incident failed to demonstrate abnormal exposure

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to fluorides by inhalation or ingestion. It was concluded that, as the concentration of fluoride found in the atmosphere was relatively low and as no evidence of chronic effects was found, the possibility is slight that toxic concentrations of fluoride accumulated during the October 1948 episode.

In the winter of 1931-32, during an examination by Flemming Møller and Gudjonssen (59) of workers in Copenhagen for silicosis, the X-ray revealed a peculiar sclerotic bone affection in cryolite workers. In pronounced cases, the affection had attached all the bones of the organism, but particularly the vertebral column and pelvis. The investigators assumed the affection to be fluoride poisoning caused by the cryolite dust. The gastric symptoms were considered due to a slight corrosion of the mucous membrane of the stomach from the liberation by the hydrochloric acid of the stomach of hydrofluoric acid from the dust swallowed. The bone changes were considered due to absorption and the resulting deposition of calcium fluoride in the bones. Experiments on rats revealed that cryolite is toxic, but symptoms identifiable with either the acute or chronic poisoning were not observed.

Slagsvold (60) reported the presence of disease in cattle grazing around Norwegian aluminum works. The symptoms were loss of appetite, emaciation, and anemia, Conjunctival irritation occurred with photophobia. The gait was stiff and painful and bone fractures were common. The cows yielded little milk. Sheep had thin, stiff wool that fell off considerably in winter. In both animals, especially in sheep, chewing was impaired. The grinding surfaces of the molars wore irregularly and formed sharp points corresponding to hollows in the opposite teeth. In air-dried hay from the district as much as 25 mg. fluorine in 100 grams was found. It was possible to show experimentally that the affection was due to fluoride ingestion (61).

In 1935 Bardelli and Menzani (62) reported that since 1929 damage to vegetation, failure in the cultivation of silkworms, and disease among herbivora of the character described above had been observed around an aluminum factory in northern Italy. Air-dried hay from the neighborhood contained an average of 59.3 mg. of fluorine in 100 grams, compared with 14 mg. in control hay.

A peculiar condition of the teeth in different parts of the world, referred to in the United States as mottled enamel, has been mentioned at various times in the earlier literature, but the trouble was not definitely connected with exposure to fluorides until in 1916 Black and McKay (63) reported the results of their study of the disease in Colorado. A similar dental disease called darmous, which attacks the permanent teeth, of animals especially but also of human beings, occurs in North Africa (Algeria, Tunisia, Morocco). The disease is endemic in certain States of the United States, in South America, China, Holland, France, Spain, Italy, Mexico, South Africa, Bahama, and the Cape Verde Islands (64). The first description of its occurrence was published by Velu (65) in 1922, although it was known earlier. Velu showed that it was not a local dental disease but a general chronic intoxication by fluoride as a result of drinking water that had passed through beds of phosphorite having a high fluorine content. The disease did not occur in places where the fluorine content of the soil was lower than 20 mg. in 100 grams.

In 1928 Kaminski (66) reported the complaints of workers in Petersdorf (mostly those engaged in etching glass) of the roughness of their teeth due to exposure to hydrogen fluoride gas fuming in air, which irritated the mucous membranes and injured the enamel of the teeth. He was asked frequently by the workers to whiten their teeth. He stated that the cause of the discoloration was the death of the pulp and the consequent loss by the dentine of its transparency due to effusion of blood into the pulp cavity, discoloration of the teeth appearing almost immediately.

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According to Greenwood (19) biological interest in fluorine compounds is due essentially to the following observations: (a) The consumption of a drinking water containing 1 part per million, or more, of fluorine during the calcification of the teeth causes hypoplasia of the teeth (mottled enamel) in man and lower animals; (b) feeding certain phosphatic mineral supplements containing considerable quantities of fluorine compounds to domestic animals has affected them adversely; (c) small quantities of fluorides retard fundamental enzymatic processes; (d) in the United States, the use of fluorine compounds (cryolite and barium fluosilicate) as insecticidal sprays for fruits and vegetables has been expanded.

In 1943 Brodie (67) reported that animals on farms to the south and east of the aluminum factory at Fort Williams, Scotland, were markedly emaciated, apparently from the effects of an excessive intake of fluorine. This fact, with the recognition that large quantities of fluorine compounds were escaping into the atmosphere from the factory and that dental changes were reported among some school children in the area, led to the appointing of a fluorosis committee (67) in 1945 to study the health hazard to man and animals.

Although, aside from the serious impediment to economic methods of sheep and cattle farming in the area, the residents in the neighborhood of the factory showed no signs of injury to health, the statement (67) is made that it is important that everything practicable should be done to reduce the amount of fluorine discharged from the factory.

According to Williamson (68) the dental signs of fluorosis observed in the population of Kenya, East Africa, are sufficient proof to warrant a full inquiry and survey on the following lines: (a) To check and analyze regularly all domestic water supplies; (b) to survey and map in detail endemic areas; (c) to undertake rock analyses for correlation; (d) to correlate the caries incidence with dental fluorosis in East Africa; (e) to publicize possible serious effects of fluorides from a public health point of view; (f) to take adequate steps to reduce concentrations of fluorides in domestic water supplies to less than 1 p.p.m.; and (g) to investigate the possibility of skeletal changes in the indigenous population.

The geological structure of Kenya is such that one would expect high fluoride figures. Large areas of the country are covered by formations from comparatively recent volcanic action. The surface waters pass through the soil, which in many areas consist of a high percentage of volcanic ash, and then pass through the weathered trachyte tuffs or lavas (68).

Effects of Fluorine Compounds on Plants

Fluorine is found in a constant manner in plants as well as in animals. According to Truhaut (16) fluorine was distinguished in plants for the first time in 1845 by Muller and Blake (16) who discovered it in grains of barley. In 1852 Wilson (16) found it in a whole series of plant species. It was discovered in fossil wood and coal successively by Rogers, Mene, and Phipson. Later, Leperre and Pondal found it in raisins (16). Gautier and Clausmann (16) examined 67 plant samples represented especially by edible plants.

As regards the organs (16), the highest content of fluorine is found in the leaf, as is the general rule for the other elements existing in traces in plants; the lowest content is found in the stems, wood, and bark. The fruit and the seeds present an intermediate content; it should be noted, however, that there is an accumulation of fluorine in the skin of the fruits. In the banana 5.10 mg. have been

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found per 100 grams of dry skin, compared with 0.38 mg. for the rest of the fruit. Tea is particularly rich in fluorine - 41 to 60 mg. per kilogram. Reid (16) confirmed this statement for China tea in which he found up to 175.78 mg. of fluorine per kilogram of dry substance, although other edible plants contain only 0.20 to 8.5 mg. fluorine per 100 grams of dry substance. According to Lockwood (16), 82 to 97 percent of the fluorine in tea is found again in the aqueous infusion.

Naturally the content of the soil in fluorine influences the amount of this element in the plants that are cultivated thereon. Gaud, Charnot, and Langlais, quoted by Truhaut (16), obtained per 100 grams of dry matter 7.42 mg. of fluorine in samples coming from soil containing 0.016 percent of fluorine and 20.9 mg. from samples coming from soil containing 0.06 percent of fluorine. This is interesting from the toxicologic point of view for in the last instance the authors (16) noted signs of chronic fluorine intoxication in cattle, which were absent in the first.

Plant disease due to chemicals such as hydrogen fluoride in any given area is a continuing process paralleling disease caused by living organisms. Physical appearance is not enough to distinguish fluorine injury to plants; the symptoms must be correlated with other facts, including a high fluorine content of the tissue. Diagnosis based on symptoms alone is not always possible (69).

Hydrofluoric acid gas produces symptoms similar in some respects to those produced by sulfur dioxide. Both produce injury to marginal and interveinal tissues of broad-leafed plants, and the symptoms on evergreen plants are similar.

Similarities exist (69) between the symptoms designated as blights, scalds, scorches, leafspots, shotholes, blotches, silvering, tip burns, and chlorosis, and the symptoms of disease owing to phytotoxic gases such as hydrogen fluoride. The effects on the plant, of which the symptoms constitute the evidence, are relative in character, shaped by many factors such as concentration of gas, time, temperature, humidity of the air, age, light, nutrition, water relations, and varieties. This is not to question the existence of symptoms that are characteristic of chemically induced diseases. The symptoms of such diseases are as positive as those of other diseases, and, when typically present, may be depended on with confidence (69).

According to MacIntire (70), soils possess distinctive capacities to fix additive fluorides against rainwater leaching and against migration of the fluorine ion into above-ground forage crops and such migration is repressed in soil systems that contain adequate supplies of calcium.

From studies made in Tennessee, MacIntire (70) concluded that fluoric contamination of forage vegetation came directly from the fluoric effluents in the atmosphere, rather than through uptake of fluoride from the soil.

Daines (71) and collaborators found that distribution of fluorine throughout a plant is characteristic of the method of fluorine application. In plants subjected to fumigation there was a high fluorine accumulation in the leaves, whereas the stems and roots showed very little increase, if any, above normal for these tissues.

Plants treated with NaF through the roots revealed the greatest fluorine accumulation to be in the roots, the leaves containing abnormal amounts but not as much as the roots. Stems generally were low in fluorine content.

From the results of fumigation experiments, it appeared that of all the plants studied (72) sweet potato, white pine, peach, and gladiolus were the most sensitive,

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being injured at concentrations of 0.01 to 0.1 p.p.m. of fluorine in the fumigation chamber. Tomato, which consistently escaped injury at 0.1 p.p.m. of fluorine and below, showed definite signs of injury at 0.31 p.p.m. Spinach, pepper, and corn were injured at concentrations of 0.4 to 0.5 p.p.m. of fluorine.

In general, fluorine toxicity symptoms resulting from the absorption of fluorine from the atmosphere through the foliage had the same appearance as those produced by the absorption of fluorine through the roots from the nutrient (sand and solution) substrate. Mild fumigations caused injury chiefly to the younger fully matured leaves, appearing as tip or marginal necrotic areas, which with time became bleached to a buff color. As a rule, the older leaves were unmarked. As a result of heavy fumigations, symptoms of fluorine injury differed from those already described. All leaves regardless of age were affected. Some plants such as tomato, when exposed to high concentrations of fluorine in the atmosphere, underwent a preliminary wilting and developed water-soaked areas, which on desiccation assumed a typical buff color. Older portions of the plant had such necrotic areas scattered over the leaf surfaces whereas in the younger leaves they were confined to the tips and margins. Fluorine analyses of the foliage of fumigated plants revealed abnormal amounts of fluorine in the tissue. For example, tomatoes fumigated at 0.47 p.p.m. of fluorine for 3 hours accumulated as high as 600 p.p.m. of fluorine in the leaves.

Utilizing the fig as experimental plant, Gaud and his collaborators (16) studied the distribution of fluorine in the various organs in subjects produced in countries with inhabitants unaffected by fluorine and in countries in which darmous is found. With figs produced in the former, it is the leaves that have the highest amount of fluorine (44.5 mg. per kg. of dry material). With the fig produced in countries where darmous is prevalent, the root bark contained much more fluorine (135.40 mg. per kg. of dry material) than the rest of the plant; next, in decreasing order of richness in fluorine, the leaf (93.60 mg.), the bark of the stem (18 mg.), and, finally, the wood of the root (7.2 mg.).

Gaud (16) expressed the hypothesis that the leaves, which are required to fall, and the bark, which scales off under the form of wrinkles, with a plant affected by fluorosis, will play a role of disintoxication analogous to appendages (hair and nails) in the animal.

Griffin and Bayles (72) fumigated several species of growing plants, including peach, apple, wild black cherry, Norway spruce, buckwheat, tomato, and corn, with relatively low and moderate concentrations of hydrofluoric acid gas to determine concentrations that might cause injury to various species, the appearance and character of injury, and the absorption of fluorine by plants. They (72) found that the injury caused by fumigation with toxic acid gases is influenced by such variables as relative humidity of the air, soil moisture, sunshine, age, and physiologic activity of the plant and of the leaves.

The experiments (72) showed that the leaves of peach, wild black cherry, buckwheat, tomato, and corn are very susceptible to acute damage when exposed to small amounts of hydrofluoric acid in the air. Apple foliage is less susceptible. Exposure of peach trees for a few hours to hydrofluoric acid gas concentrations as low as 0.05 to 0.1 p.p.m. may cause acute damage to a small percent of the leaves, but higher concentrations or longer exposures are required to cause twig or shoot damage.

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Effect of Fluorine Compounds on Animals

Peirce (73) reported that in very early records, dated 1100 A.D., attention was called to a disease of domestic animals, particularly of grazing sheep, which generally appeared after the periodic volcanic eruptions that have been an important feature of the history of Iceland. In connection with this statement it is interesting to note that in the area of the Katmai volcano alone an estimated (74) 135,000 metric tons of fluorine is released yearly in the form of gaseous hydrofluoric acid.

Fluorine in the animal world is said (16) to have been distinguished first in 1803 by Morichini. The discovery by this Italian author of fluorine in the teeth of a mammoth exhumed in the Roman country was the "wonder of the epoch."

Carnot is mentioned by Truhaut (16) as having found much more fluorine in fossil bones than in the bones of living animals. The amount of fluorine in fossil bones of dead bodies is so high that it does not seem possible that the fluorine had existed in such concentrations in the living animal. The hypothesis (16) is that the deposits of prehistoric animal bones correspond to the origin of phosphate deposits rich in fluorine, resulting from a hecatomb owing to sudden appearance of massive epidemics of fluoroses, which could be explained by volcanic eruptions accompanying geologic transformations. It has been noted that volcanic lavas and fumes are rich in fluorine. The role of volcanic eruptions in the etiology of fluorosis is still actually being manifested in certain regions of the globe, the islands in particular (16).

Fluorosis was described in the records of an outbreak subsequent to the 1845 eruption of Hekla (73). Although many animals died of acute poisoning within a few weeks of this disturbance, most of them suffered no apparent trouble until the following year when symptoms of emaciation, decreased milk yield, weakness and impairment of the use of the limbs, thickening of the joints, and the development of exostoses of the long bones and the jaws became apparent. Young animals suffered most. Mottling of the teeth with selective abrasion of the molars and pitting of the incisors were also described. All but the dental symptoms were reported to subside if the animals were confined in barns and fed on hay produced before the eruption. The skeletal changes, which are not generally accepted to be typical of chronic fluorine poisoning, have since been recognized by Roholm (73) in museum collections of material preserved since the 1845 outbreak.

The occurrence of a similar disease among animals grazing in the neighborhood of various factories appears to have been ascribed to fluorine in 1912 (73). The industries quoted by Peirce (73) as principally incriminated are those producing superphosphate, hydrofluoric acid, glazed bricks, copper, aluminum, glass, and enamel. All such factories either emit effluents of hydrogen or silicon fluoride or give rise to dust containing fluorine.

Blakemore, Bosworth, and Green (74) describe the occurrence in England of fluorosis in farm animals arising from industrial contamination of pasture in connection with brick manufacture, the calcining of ironstone, and the fumes from a color and enamel factory. Levels of pasture contamination of 7 p.p.m. to 90 p.p.m. are shown on a map with discussion of the severity of clinical symptoms in animals. Representative clinical cases are recorded, and the histology of skeletal changes is illustrated by microphotographs.

Urinary analysis was found (74) to be a convenient way of diagnosing fluorosis, especially in subclinical cases where no dental signs or obvious skeletal changes

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were present. The value of this simple method is emphasized for surveying areas of potential fluorine hazard in respect to either human or animal population.

In 1943 a farmer in Inverness-shire, Scotland, in the neighborhood of one of the factories manufacturing aluminum by an electrolytic process, noticed that his animals were suffering from an unusual form of debility in spite of an abundant supply of herbage. The farms in the vicinity were visited by a veterinary advisor of the area. He reported marked emaciation among animals to the south and east of the factory: this was due to dental abnormalities, which prevented proper mastication. The changes in the teeth were attributed to prolonged ingestion of fluorine compounds (67).

A formal request was made by the Secretary of State for Scotland to the Medical Research Council to investigate the matter. The Council appointed a Fluorosis Committee.

The report (67) of the Fluorosis Committee deals first with studies of the contamination produced in the vicinity of the factories by fluorine compounds; with a description of the topography, meteorology, geology, and vegetation; the manufacture of aluminum by the Hall-Heroult process is described and diagrams of the factories and the arrangement of the furnaces are given; methods are described of sampling the great variety of materials for laboratory examination, including human blood and urine; air samples at various processes in the factories and at different situations outside the factories up to 7 miles in the direction of the prevailing wind; samples of soil, grass, and water; and specimens of the milk of cows and ewes, of cow urine, and cow and sheep organs, and human teeth. Inside the factory the concentration of fluorine reached 3.60 mg. per cubic meter in one of the furnace rooms. The concentrations outside the factory are compared with the average found in the furnace rooms; they ranged from 15 percent of furnace room concentration 200 yards from the factory to about 3 percent 1 mile away. Samples of dried soil close to the factory had a fluorine content of about 1,010 p.p.m., and 7 miles away in the direction of the prevailing wind the content was about 66 p.p.m. Analyses of grass samples ran parallel with those of the soil.

Dental fluorosis affecting both cattle and sheep was established, and the dental lesions were confined in animals reared on the contaminated pastures; cases of osteomalacia also were found. Loss of condition of cows and lowered milk yield were severe, but the fluorine content of the milk was not raised materially.

The physical properties of bones from affected animals were studied by mechanical, chemical, and crystallographic tests. The mean value for fluorine in affected bones was 1.02 percent, and in the controls 0.028 percent of the ash (67).

Effects of Fluorine Compounds on Man

Fluoride poisoning may be acute or chronic. Data on the subject reveal (64) that the form of fluorine used, the method and length of time of administration, and individual susceptibility vary the toxic effects so much that comparison of the data is scarcely warranted.

Acute Poisoning

Acute irritation of the gastrointestinal tract, such as vomiting (often with blood), diffuse abdominal pains, and diarrhea, appear very soon after ingestion of soluble fluorides. Symptoms due to absorption occur after varying, usually short,

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periods as alternating convulsions or spasms and paresis, which may be localized or general. The spasms are very painful with pains and paresthesia in the extremities. Between the spasms general weakness and sluggishness are present. Various other less constant symptoms given by Roholm (49) are rise in temperature, difficulties in speech and swallowing, in coordinated movements of the eyeballs, thirst, salivation, and perspiration. In most cases death occurs after a few hours under prostration, dyspnea, and failing pulse. Consciousness is unaffected.

When the intoxication is not fatal, there are signs of toxic nephritis (albumin, blood, and casts in the urine).

A single subcutaneous injection of sodium fluoride in the rat produces disturbance in the formation of the teeth, which, according to Roholm (49) appears macroscopically on the incisors after about 4 weeks as a circular, distinctly delimited band of white, unpigmented enamel. Subacute poisoning is manifested in the rat by the development of a cachectic condition with spontaneous hemorrhage from the mucous membranes.

The effects of gaseous fluorine compounds is known only from rather limited material (32), local irritation of the mucous membranes predominating. Dyspnea seems to be the principal symptom in man. The acute toxic effects experienced by employees exposed to fluorides in a beryllium plant (29) were respiratory diseases and dermatitis.

The following characteristic symptoms have been listed by McClure (64): A condition of drowsiness and weakness resulting from paralysis of the vasomotor centers; cramps (epileptic in character), which may attack a single organ or the entire body; paralysis of the vasomotor centers; acceleration and deepening of the breathing, with paralysis following; vomiting; secretion of the salivary and tear glands, which is not stopped with atropin; early rigor following death. According to McNally (75), rabbits dusted daily with a mixture of 1/2 ounce sodium fluoride and 5 pounds silica dust suffered loss of weight, stiffness of the vertebral column, and finally paralysis of the spinal cord.

Sollman (76) has stated that acute poisoning presents chiefly the phenomena of acute gastroenteritis and collapse and may run a rapid course, with sudden nausea and vomiting, abdominal burning, and diarrhea for 3 to 6 hours, and stupor and weakness for 36 hours in sublethal cases. Fatal cases develop muscular weakness and tremors, progressing to clonic convulsions originating in the cord and higher centers, fall of blood pressure, general collapse, sometimes with grayish-blue cyanosis, dyspnea, and arrest of respiration and of the hearth. Death may occur in a few minutes or may be delayed for 10 hours or longer (76).

According to Williams (31), with exposure to concentrations of fluoride fume of over 100 mg. per 10 cm., a severe "biting" sensation is experienced in the nose, followed within a few minutes by a "running nose" with discharge of considerable fluid. After about 20 minutes, blood may show on blowing the nose. This may persist for several days and in some persons may recur almost indefinitely. These effects are rarely important enough to report to the plant hospital.

Chronic Poisoning

In spite of the voluminous literature on the effects of exposure to fluorine on vegetation and animals and the demonstration of chronic fluoride poisoning in a dog by Brandl and Tappeiner as early as 1889, chronic fluoride poisoning in man is said not to have been known until it was discovered in 1931 by Møller (77) while

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he was investigating silicosis among workers in a cryolite factory. Radiological examination of the men for silicosis revealed peculiar changes in the bones of some. It was this discovery that led to the researches by Roholm (49) and the publication of his comprehensive work on fluoride intoxication.

The symptoms of poisoning in the men examined by Møller (77) corresponded clinically and pathologically with those found in animal experiments and the radiologic findings obtained during life tallied with the post mortem examinations made by Roholm (49) on two cryolite workers.

Effect on dental and osseous tissue. - Attention was first called to "an endemic development imperfection of the teeth heretofore unknown in the literature of dentistry" by Black and McKay (63) in 1916. This condition they termed "mottled teeth." McKay (78) was the first definitely to associate the etiology of this condition with something in the drinking water. In 1925, he (79) persuaded the community of Oakley, Idaho, where the incidence of mottled enamel was 100 percent, to obtain its water supply from a nearby area where mottling had not been found. Another survey after 8 years revealed no mottling in the permanent teeth of the children born after the change had been effected. Chemical analysis of the water showed that the drinking water from the first source contained 6 p.p.m. of F and that from the second source 0.5 p.p.m. of F.

It was not until 1931, however, that fluorine was demonstrated definitely by three independent studies (78) as the etiological factor in the mottling of the enamel. Churchill (80) found 2 to 13.7 p.p.m. fluorine in water in endemic areas where mottling was observed. Smith, Lantz, and Smith (81) confirmed Churchill's findings and demonstrated it experimentally in white rats. In the same year, Balozet and Velu (82) made similar observations in the rock phosphate areas of North Africa.

Changes in the teeth during the time of their formation in children are among the most easily reproducible and recognizable of all the symptoms of damage by ingested fluorides. These changes have been studied by many investigators, whose results are in general agreement. Fluorine has a detrimental effect upon the growth of the teeth and the parts of a tooth calcifying during the period of too high fluorine intake will acquire permanent defects; however, teeth or parts of teeth that are already calcified do not change with the administration of fluoride, except in high concentrations.

Roholm (49) observed the following effects upon the teeth of rats exposed to fluorine. Rats are particularly valuable for this purpose as their incisors grow continuously from a persistent pulp. With the lowest concentration of fluorine that causes a visible effect, the incisors of the rat lose the pigment that normally causes their dark-orange color. The enamel becomes lighter, loses its luster, and finally becomes chalky white. Higher concentrations cause localized hypoplasia (defective formation) of the enamel, which becomes less resistent and chips off. The strength of the teeth is reduced markedly, and the sharp, chisel-like cutting edge of the incisors wear off. Sometimes the teeth are worn off down to the gums. All incisors are elongated, especially in the upper jaw, where they curve back and may penetrate the roof of the mouth.

The lowest degrees of fluoride effect (49) produce alternate rings or bands of pale pathological enamel and dark normal enamel. Often the rings are arched, with the concavity towards the point of the tooth. The same phenomenon is observable (49) when sodium fluoride is added to the drinking water. Intermittent injections

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of sodium fluoride cause the development of alternating bands of pathological and normal enamel - a light and a dark layer for each injection.

Although mottled enamel is undesirable cosmetically, there is evidence that the affected teeth are less likely to become carious. Osteosclerosis due to fluorine, however, appears not to have any such virtue (83).

Concurrent with the pigmentation of the teeth, there may be destruction of enamel and dentine, starting with chalky white deposits in the early stages progressing on through pitting and erosion to almost complete destruction (84).

The most interesting and probably the most significant symptoms of fluoride poisoning, from the health standpoint, are the changes in the osseous system. After absorption, part of the fluorine is stored in the body, especially in the bones and teeth. Fluorosis can effect bone at all ages, but only influences tooth structure during development (85). This fact was first established by Brandl and Tappeiner (86) in an experiment on a dog. The condition was first noted in man by Møller (77) in 1931. As mentioned previously, Møller observed a peculiar appearance of the bones of men he was examining radiologically for silicosis. Roholm (77) found several bone changes in all cryolite workers examined who had been exposed to excessively high concentrations of dust. He summarized the result of his radiologic examination as follows:

> The first thing to emphasize is the fact that the affection is a system-disease, for it attacks all bones, though it has a predilection for certain places. The pathological process may be characterized as a diffuse osteosclerosis, in which the pathological formation of bone starts both in periosteum and in endosteum. Compacta densifies and thickens; the spongiosa trabeculae thicken and fuse together. The medullary cavity decreases in diameter. There is a considerable new formation of bone from periosteum and ligaments that normally do not calcify or only in advanced age undergo a considerable degree of calcification. All signs of bone destruction are absent from the picture.

According to Larner (84) the affinity of fluoride for hard structures is exemplified by its effects on bones, where it tends to accumulate, leading to hypercalcification and brittleness. Ligaments and tendons also become calcified. Serious symptoms may ensue such as loss of mobility of joints, easy fracture, and pressure on the spinal cord. In children it may interfere with normal bone formation. The similarity of this syndrome with the disease spondylitis deformans has been pointed out (84).

In more than half of the 35 workers examined clinically by Roholm (49), motility in columna (ability to move the spinal column spontaneously) was restricted, both flexion-extension and rotation. The workers were divided into three groups according to the degree of restriction. In the slightest cases there was merely a little stiffness of the lumbar and thoracic parts with slight restriction of extension and rotation; 21 persons belonged to this group. The lumbar and dorsal but not the cervical region of the moderate cases was rather markedly rigid. It was possible for them, as a rule with some difficulty, to pick up an object from the floor by bending the knees; there were 10 workers in this group. Among the most severe cases (four elderly men), there was virtually complete rigidity of the entire spine and more or less pronounced restriction of head movements. This was particularly marked in a 57-year old male worker, who had been employed at the factory for 12 years. The head

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was fixed in a bent-over position; movement was possible only to an extent of 5° to 10° in both sagittal and frontal planes. To look sideways, he had to turn the whole body. This man was unable to pick up anything from the floor by bending the knees and could not put on his socks without aid.

On the whole, the restriction of movement was found by Roholm (49) to parallel the osseous changes. It was noteworthy, however, that only some of the workers whose motility in columna was moderately restricted complained of stiffness. Even those most severely affected complained of surprisingly little inconvenience therefrom.

The most common chronic clinical symptoms of which the employees examined by Roholm (49) complained were various dyspeptic phenomena, shortness of breath, and rheumatic attacks. The gastric symptoms (loss of appetite, nausea, vomiting, and cardialgia) were experienced by 80.9 percent of the workers. The first three symptoms were definitely connected with the work and were experienced for a few days or weeks after beginning work in the dusty atmosphere. Thereafter some of the workers tolerated the dust, whereas others still had transitory symptoms after holidays or if the dust content of the air increased temporarily. Seven of the workers complained of continuous constipation or constipation alternating with diarrhea, which was more or less definitely connected with working in dust. Twenty-two workers complained of chronic gastrointestinal symptoms.

Fifty-one percent of the workers complained of circulatory and respiratory symptoms. Dyspnea was the most frequent symptom, usually moderate in degree on exercise but increasing in severity during exposure to thick dust.

More than one third of the workers complained of indefinite rheumatic pains and stiffness in the body that, with more or less justification, could be connected with affections in bones, joints, or muscles.

The most frequent nervous symptoms were tiredness and indisposition, which were experienced by 15 employees - 12 men and 3 women.

Table 5, compiled by Truhaut (16) summarizes the figures from various authors on the fluorine content of bones and teeth of normal persons.

Truhaut (16) concluded that (a) the content in bones and teeth, in man and animal, is about the same, containing most often between 0.1 and 1.5 mg. per 1,000 grams ashes; (b) the dentine or ivory contains more fluorine than the enamel, some authors utilizing spectographic technic even claiming not to reveal the least trace of fluorine in the enamel of normal human teeth; (c) the amount of fluorine increases very clearly with age; (d) the milieu influences considerably the content of fluorine, the teeth and bones of marine animals containing about 10 times more fluorine than terrestrial animals. This last fact should be related to the richness of sea water in fluorine and a relationship has been shown between the content of fluorine of the bones and teeth and the amount of this element in the drinking water. In fact, the bony and dental tissues realize, in the case of fluorine, an accumulation comparable to that of the thyroid gland foriodine. By using radioactive fluorine, this accumulation has been verified by physical passage. Truhaut (16) emphasizes that it is favored by the insolubility of calcium fluoride and also by the well-known affinity of fluorides for the phosphates with which they tend to form fluophosphate complexes, of which apatite is a type.

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TABLE 5. - Content of fluorine in the bones and teeth of normal individuals

Authors	Years	Fluorine in mg. per gram of dry material (DM) or of ashes (A)	Species
Bethke	1929	1/ DM 0.231-0.409	Pig femur
		.59	bone in skull
		.70	Man bone of members
		.30	teeth
Klement	1933	1/ A .38-0.65	Various animals : bones
		8.00-16.2	Marine animals bones
		6.90-7.40	teeth
Chang	1934	1/ DM .5376	molars
		.6225	Cow dentine
		.2666	enamel
		.5840	bones
Roholm	1937	1/ A .48-2.10	sides
		.19-0.30	Man teeth
		.044-0.57	enamel
		.30-0.31	dentine
		.12-0.38	Young animals : bones
		.18-0.81	Old animals : various bones
		.32-0.34	Young mammals : bones
		4.40-6.50	Old amphibians : bones

1/ DM = dry material; A = ashes.

Truhaut (16) answers the question "Under what form does fluorine exist in the osseous and dental tissues?" as follows:

> This problem has been studied by Klement and Tromel, Dallemagne and his collaborators, with the aid of physical methods (spectrums of diffraction to X-rays, measures of refractive indexes) combined with chemical analysis. These authors conclude on the presence in the dental enamel of a micro-crystallized complex of the type of natural apatite of the general formula $3_2(PO_4)_2\ Ca_3 + X_2\ Ca$ in which $X_2\ Ca$ may be F_2Ca (fluorapatite, $(OH)^2\ Ca$ (hydroxyapatite), or $CO_3\ Ca$.
>
> For a long time one had thought, following Hoppe, that such a complex existed likewise in the bones as well as in the dentine or ivory and the cement of dental tissue. But the researches of Dallemagne and his collaborators completed by those of Cartier, who has studied the solubility of these tissues in function of pH, lead to think that in the dentine, and the cement, as well as in the osseous tissues, the mineral element is constituted by a mixture of tricalcic phosphate, calcium carbonate, and calcium fluoride not combined among them under the form of complex of the apatite type.
>
> Consequently, only the enamel will contain fluorapatite, besides hydroxyapatite, and will thus be opposed - by its mineral composition and also by the presence, in its organic woof, of a protein very

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particular, very resistant to chemical agents and is apparent to the keratin of the appendages - at the same time to the osseous tissue and to the dentine and to the cement. In making the enamel a calcified tissue of special structure, these researches explain its particular hardness and its resistance to chemical and mechanical agents.

HYDROGEN FLUORIDE

Hydrogen fluoride, (common names being hydrofluoric acid and anhydrous hydrofluoric acid) formula HF or (H_2F_2), is one of the most important and best known compounds of fluorine. It is clear, colorless, fuming, and corrosive with a molecular weight of 20.01, melting point of -92.3° C., specific gravity of 0.9879 at 12.5° C., and density of 0.713 (air = 1). It solidifies at 82.9° C. and boils at 19.5° C. The most characteristic property of hydrofluoric acid is its ability to dissolve glass, and, because of this, it must be kept in platinum, wax, or hard rubber and must be prepared in platinum or lead vessels (87).

It has extensive uses in the glass industry, in making opalescent electric light bulbs or fluorescent tubes for neon signs, as well as in glass etching in the ceramic industry; in the manufacture of fertilizers; in the electrolytic production of aluminum; and in magnesium foundries (88). Anhydrous hydrogen fluoride is used extensively by the petroleum industry in the synthesis of high octane gasoline by alkylation and in the manufacture of aluminum fluoride, which is of importance in the commercial production of metallic aluminum. Considerable quantities of hydrogen fluoride are used to make artificial cryolite, refrigerants, and insecticides and in the electrolytic refining of metals, the pickling of metals, electroplating operations, and the etching of glassware (87).

Toxicity of Hydrogen Fluoride

Hydrofluoric acid is poisonous and corrosive in either the liquid or vapor form. Small amounts in the eye can cause intense irritation of the eyelids, lachrymation on inhalation, and slow ulceration of the conjunctivae. Large amounts in the eye cause immediate blindness. The vapor or liquid material is very dangerous when in contact with any part of the body or if ingested orally (48). Subcutaneously its destructive action affects the tissue and blood vessels.

Chronic poisoning by hydrofluoric acid has not been recorded. Machle and coworkers (89) found from their animal experiments on the inhalation of high concentrations of hydrogen fluoride that exposure to atmospheres containing 1.0 to 1.5 mg. hydrogen fluoride per liter produced death in a significant proportion of animals exposed for 5 minutes or more. Concentrations at or above this level may be considered dangerous for exposure of any duration. Although no deaths occurred in two groups exposed to 0.79 and 0.50 mg. per liter, respectively, for 5 minutes, 7 to 10 of these animals killed for necropsy 25 hours to 55 days after exposure revealed the typical pathological lesions. One animal killed after 25 hours had elapsed and two others killed at the end of 4 months were considered normal. One rabbit killed 6 days after a 30-minute exposure to 0.56 mg. per liter revealed the usual evidences of damage, whereas another rabbit examined 4 months after the same exposure was like the controls.

Exposure for 6 hours to atmospheres of 0.044 mg. per liter caused no deaths, though some evidence of liver and kidney damage was seen in 3 animals examined within 22 days following exposure.

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One rabbit examined 18 hours following 41 hours of daily 6-hour exposures to 0.0245 mg. per liter had suffered considerable liver and kidney damage, with some evidence or an early fibrosing process in the emphysematous lungs. This concentration, although too low to cause death, is unsafe for prolonged exposure.

Exposures to concentrations of hydrogen fluoride above 1.5 mg. per liter for any period is dangerous for rabbits and guinea pigs.

Concentration of 1.0 mg. per liter and less caused no deaths in rabbits and guinea pigs exposed for as long as 30 minutes, although evidence of injury were definite.

Concentrations below 0.1 mg. per liter were tolerated by rabbits and guinea pigs for 5 hours without injury severe enough to produce death; 0.0245 mg. per liter caused no deaths in 6 animals exposed for 41 hours.

Machle and Kitzmiller (90) referred to available data that indicate that the lower limit of toxic concentrations of hydrogen fluoride in air lies between 0.03 and 0.0025 mg. per liter. The preceding paper in this study (89) demonstrated that the level lies below 0.0245 mg. per liter. Although no animals (of a group of 3 rabbits and 3 guinea pigs) died within a year following 41 hours of daily 6-hour exposure at this level, the pathological findings on those sacrificed for necropsy revealed varying degrees of damage. Accordingly, the concentration of exposure atmospheres was lowered to 0.0152 mg. per liter. This concentration, though slightly irritating, was found to be tolerable and respirable, and it is therefore a level at which chronic human exposure could easily occur. Higher concentrations are irritating enough to discourage prolonged human exposure.

Table 6, giving lethal concentrations of hydrogen fluoride by inhalation was prepared by Roholm (54) from data in the literature.

TABLE 6. - Lethal dose of hydrogen fluoride, in milligrams per liter

Death after 5 minutes respiration of 1.5 HF per liter	- Rabbit and
Death after 1/2 - 1-1/2 hours respiration of 0.6 HF per liter	- guinea pig
Death after 1 day respiration of 0.03 HF per liter	- Guinea pig
Tolerable for several minutes, but unpleasant, 0.026 HF per liter	- Man

Skin Injury From Industrial Exposure to Hydrogen Fluoride

Hydrofluoric acid is intensely caustic to mucous and skin surfaces. Stanton and Kohn (91) reported that contact of the skin with the anhydrous liquid produces severe burns that are felt immediately. Concentrated aqueous solutions also cause an early sensation of pain, but more dilute solutions may give no warning of injury. If not promptly removed, the skin may be penetrated by the fluoride ion, leading to the later development of painful ulcers, which heal slowly. A 0.03 percent solution of sodium fluoride will destroy epithelium. This observation suggests the necessity for preventing the diffusion of the fluoride ion in treating serious burns (91).

Internal Injury From Industrial Exposure to Hydrogen Fluoride

In addition to causing deep burns on skin contact, hydrofluoric acid also acts as a protoplasmic poison. The fumes or mist of this acid on inhalation have been found to act as primary irritants and continuous exposure to an atmosphere contaminated with even low concentrations causes severe inflammation and congestion of the respiratory tract. This may result in pneumonitis (87).

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When swallowed, hydrofluoric acid will immediately cause severe irritation of and damage to the esophagus and the stomach. Severe irritation to the respiratory tract will also occur (92).

Permissible Limits of Hydrogen Fluoride in Air

The threshold limit value for hydrogen fluoride as adopted by the American Conference of Governmental Industrial Hygienists in Los Angeles, April 1953, is 3 parts per million parts of air.

According to Shilen, Galloway, and Mellor (29), however, any statement of hydrogen fluoride in terms of parts per million at temperatures below 90° C. is ambiguous. Below 90° C., hydrogen fluoride is not the simple molecule H_1F_1 but is an associated molecule of one or several multiples of H_1F_1, sometimes stated as H_nF_n. Shilen and co-workers (29) quote Treadwell and Hall as saying that the acid is bimolecular up to +40°, but above +80° it is monomolecular. Between these temperatures, both HF and H_2F_2 molecules are present. In dilute aqueous solutions the simple molecules preponderate, but in concentrated solutions at room temperature there is considerable H_2F_2. As the molecular weight of hydrogen fluoride below 90° or 100° C. is unknown, it is impossible to state toxic limits, but it is possible and correct to do so in terms of weight per unit volume of air, as is done with the salts of hydrofluoric acid (29).

Machle and Kitzmiller (90) exposed animals 6 hours a day for 24 hours to a concentration of hydrogen fluoride of 0.0152 mg. per liter, or 15.2 mg. per cubic m. The first animal died at the end of 160 hours of exposure. Shilen and co-workers state (29) it would be reasonable to believe that the exposure when animals begin to die would be equally dangerous to humans. According to Roholm (55), man seems to be more sensitive to fluorine compounds than the experimental animals generally employed.

Referring to the experimental results of Machle and his co-workers, which showed that in a human experimental subject with a normal level of intake of fluorine from dietary sources the urinary excretion and fecal output equaled the intake within the limits of experimental error, Shilen and his co-workers (29) consider that any fluoride intake above 1.5 mg. per day is in excess of the normal that can be handled by the human body and evidently will produce some ill effect. They conclude, therefore, that any concentration that the ambiguous 3 parts per million of hydrogen fluoride may represent, and its equivalent as sodium fluoride, is too high. Three parts per million of hydrogen fluoride is too high even if the molecule were H_1F_1, but as the molecule is recognized as being associated as H_nF_n below 90° C. (194° F.), 3 parts per million of associated hydrogen fluoride raise the toxic limit from 1 to an indefinite number when calculated in terms of sodium fluoride.

In the studies by Shilen and co-workers (29), the sodium fluoride equivalent to the average of all atmospheric fluorine determinations was 0.996 mg. per cm., but at the concentrations that gave this average, cases of respiratory ailments and dermatitis reported in greatest number.

Examination of the gases and fumes evolved during electrolysis of beryllium by Hyslop and co-workers (28) indicated that the fluoride content varied throughout the experiments between 0.07 and 5.0 mg. per cu. ft. The fumes consisted of a true vapor phase and a very fine smoke or dust. Analysis of the dust revealed beryllium fluoride, beryllium oxide, barium fluoride, and sodium fluoride. With a single exception, all guinea pigs were killed within 90 minutes or less when exposed to the dust and fumes. The toxic effect apparently was due to the fluoride dust and fumes, for the elimination of any one metal from the melt did not lessen the toxicity appreciably.

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Analyses of the lungs of the animals that died or were sacrificed following exposure to the dust and fumes showed that the lung content of fluorine varied between 0 and 0.6 mg. per 10 grams of fresh tissues.

In 1940 Machle and Evans reported (93) results of a study begun in 1931 of a group of workmen exposed principally to hydrogen fluoride and to a lesser degree to the dusts of calcium fluoride in the manufacture of hydrofluoric acid. As the hazardous nature of the operation was recognized and precautions were taken to prevent undue exposure at the higher level of concentration, clinical examinations have revealed nothing significant. Determinations in 1940 of the fluorine content of the air in the center of the building gave negative results under normal operating conditions, but samples of air taken near equipment or while repairs were being made revealed 0.011 to 0.021 mg. fluorine per liter of air. The investigators concluded that exposure to these amounts eventually would result in clinical injury, as previous experiments showed that prolonged exposure to such concentrations would result in storage of fluorine in the bones.

First-Air Treatment for Injury From Hydrogen Fluoride Exposure

Speed in removing the patient from the contaminated atmosphere or removing hydrofluoric acid from the skin or eyes is of primary importance. First aid must be begun immediately in all cases of contact with hydrofluoric acid in any form. All affected persons should be referred to a physician, even when immediate injury seems slight, and the physician should be given a detailed account of this accident.

The Manufacturing Chemists' Association, Inc., 246 Woodward Building, Washington 5, D. C., in its Chemical Safety Data Sheet SD-25, adopted in 1948, on Hydrofluoric Acid reports as follows:

> General First Aid after Skin Contact with Liquid or Vapor. Workers who have had contact with hydrofluoric acid should be subjected immediately to a drenching shower of water. The clothing should be removed as rapidly as possible, even while the victim is in the shower, and medical assistance obtained immediately. It is essential that the exposed area be washed with copious quantities of water for a sufficient period of time to remove all hydrofluoric acid from the skin. Following this, an ice-cold saturated solution of magnesium sulfate (Epsom salt) or iced 70% alcohol should be applied for at least 30 minutes. If the burn is in such an area that it is impracticable to immerse the part, then the iced alcohol or the iced magnesium sulfate should be applied with compresses, which should be changed at least every two minutes; this treatment should be continued for 30 minutes. The physician should be on hand to administer treatment before the completion of the magnesium sulfate or alcohol treatment. If, however, he has not arrived by that time, it is then permissible to apply a generous quantity of paste made from powdered magnesium oxide and Glycerin U.S.P and, preferably, freshly prepared. (Oils or greases should not be applied except under instructions from a physician.)
>
> Contact with Eyes. If liquid hydrofluoric acid has entered the eyes or if the eyes have been exposed to strong concentrations of the vapor, they should be irrigated immediately and copiously with clean water for a minimum of 15 minutes. The eyelids should be held apart during the irrigation to insure contact of water with all the tissues of the surface of the eyes and lids. A physician, preferably an eye specialist, should be called in attendance at the first possible moment. If a physician is not immediately available, the eye irrigation should be continued for a second

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period of 15 minutes. After the first 15 minute period of irrigation is completed, it is permissible, as a first aid measure, to instill two or three drops of a 0.5% pontocaine solution or an equally effective aqueous topical anesthetic. No oils or oily ointments should be instilled unless ordered by the physician.

If Taken Internally. Ingestion of hydrofluoric acid causes severe burns of the mucous membrane of the mouth, throat, esophagus and the stomach. Here copious irrigation is not feasible and no attempt should be made to pass a stomach tube except by the attending physician. The patient should be encouraged to drink a large quantity of water without delay. After the hydrofluoric acid has been diluted with water, whites of eggs or mineral oil may be administered for their demulcent or soothing effect.

Inhalation. A worker who has been overcome by gaseous hydrofluoric acid must be carried at once into an uncontaminated atmosphere. A physician should be called immediately and, if a trained attendant is available, the administration of oxygen should be started at once.

In order to prevent the development of severe lung congestion (pulmonary edema), 100% oxygen should be administered as soon as possible after a severe exposure. Oxygen administration is most effective if expiration is made against a positive pressure of 6 cm. (about 2-3/8 inches) of water. This may be accomplished readily by use of a rubber tube connected to the outlet valve of a snugly fitting face mask and inserted to a depth of not more than 6 cm. below the surface of water in a suitable container. The pressure resisting exhalation should be adjusted to the patient's tolerance by varying the depth of the end of the tube below the water's surface. Oxygen inhalation must be continued as long as necessary to maintain the normal color of the skin and mucous membranes. In cases of severe exposure, the patient should breathe 100% oxygen under positive exhalation pressure for one-half hour periods every hour for at least three hours. If there are no signs of lung congestion at the end of this period, and if breathing is easy and the color is good, oxygen inhalation may be discontinued. Throughout this time the patient should be kept comfortably warm but not hot.

The Medical Advisory Committee of the Manufacturing Chemists' Association, Inc., have issued the following suggestions for medical treatment:

Treatment after Skin Contact with Liquid or Vapor. If the physician sees the patient soon after contact with a diluted solution of hydrofluoric acid (dilution 1 to 20%), there may be little or no evidence of injury. Evidence of the injury may not appear for several hours.

It is suggested that the affected area be immersed, if possible, in iced 70% alcohol solution. If it is not practicable to immerse the part, then compresses of iced 70% alcohol should be applied. The iced alcohol treatment should be continued for at least one hour as it has a tendency to relieve rapidly the pain which is usually present in this type of burn, and it is quite possible that there is a diffusion of the hydrofluoric acid from the tissues into the alcohol. As soon as there is evidence of penetration of acid beneath the skin, calcium gluconate solution (1 gm.

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of calcium gluconate in 10 cc. of water) should be injected by infiltrating the skin and subcutaneous tissues in the same manner as is used in the injection of a local anesthetic subcutaneously. All the skin which has been exposed to the acid should be infiltrated including at least 1/4 to 1/2 inches around the area. This treatment will usually prevent the development of severe burns.

After treating the affected area with either iced alcohol or iced magnesium sulfate, and after the injection of calcium gluconate solution, magnesium oxide and glycerin paste should be applied. Then the areas should be well padded with gauze and a pressure dressing applied to the area in the same manner as for thermal burns.

In severe burns, blisters filled with a sero-purulent fluid develop and the skin assumes a blanched appearance. Ten percent calcium gluconate should be immediately injected into and around the affected areas. Blisters should be cut away completely and magnesium oxide and glycerin paste applied to the denuded area for a period of 24 to 48 hours. At the end of this time, if there is no further evidence of extension of the burned area, magnesium oxide ointment should be applied.

Treatment of Burns Around Finger Nails. Burns around the finger nails are extremely painful and necessitate special treatment to relieve pain and also to prevent infiltration of the hydrofluoric acid into the deeper structures with the resulting destruction of tissues or even the bone. Eventually such infiltration may necessitate amputation.

The nails should be split from the distal end of the nail bed in order to allow free drainage. A 10% calcium gluconate solution should be injected around and beneath the nail. The affected part should then be soaked in iced alcohol or iced magnesium sulfate for 1-1/2 to 2 hours.

Contact with Eyes. Ophthalmologists may be interested in a method of treatment for chemical burns of the eye described by Ralph S. McLaughlin, "Chemical Burns of the Human Cornea," American Journal of Ophthalmology, 29:1355, 1946.

Gastric Lavage. Lavage with lime water should be instituted promptly by a physician only. If lime water is not available, milk may be used as a substitute. Soluble calcium inactivates the fluoride ion. In addition to lavage, 10 cc. of a 10% solution of calcium gluconate should be injected intravenously. Respiratory depression should be combatted with oxygen and stimulants if necessary; and artificial respiration should be used if needed.

Prevention and Control of Hydrogen Fluoride Poisoning

The most important factors in preventing injury by anhydrous hydrofluoric acid are (a) To keep the concentration in the atmosphere below 3 parts per million by volume, and (b) to prevent all contact of vapor or liquid with the eyes, skin, or gastro-intestinal tract.

The Manufacturing Chemists Association (92) presents the following preventive and control measures:

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Ventilation. The generally accepted maximum allowable concentration of hydrofluoric acid vapor is 3 parts per million by volume in air for an 8-hour working day.

Safety Showers and Eye Baths. Readily accessible, well marked, frequently inspected, rapid action safety showers must be available in the areas where hydrofluoric acid is handled. They should be capable of supplying large quantities of water under moderately high pressure. Blankets should be located near the safety showers. Special eye washing fountains, a ready source of running tap water, a bubbler drinking fountain, or a hose with a soft, gentle flow of drinking water should be available for eye irrigation. All of the above equipment should be inspected and tested at frequent intervals to insure its being in good working condition at all times. The locations of such equipment should be marked clearly.

Preplacement Physical Examinations. Chronic poisoning by exposure to hydrofluoric acid, liquid, or vapor has not been recorded. However, since the effects of a single exposure may be severe and lasting, all employees handling hydrofluoric acid should have preplacement physical examinations, and certain individuals should not be assigned to operations in which these chemicals are used. Such individuals are those with:

(a) Any form of respiratory disease.

(b) Seriously impaired vision in one or both eyes.

Periodic Physical Examinations. All employees who work constantly with hydrofluoric acid should have a careful physical examination every six months.

Employee Education. Employees working where hydrofluoric acid hazards exist should be instructed and trained in the following:

(a) Location of gas masks and other personal protective equipment, safety showers, bubbler drinking fountains, water hoses, exits, and first aid equipment.

(b) Proper use of respiratory protective devices and other personal protective equipment.

(c) The necessity for reporting any evidence, such as an unusual odor of hydrofluoric acid or any evidence of spillage of hydrofluoric acid. Contaminated areas should be flushed with copious quantities of water and the acid neutralized with soda-ash or lime as rapidly as possible. All employees engaged in this operation should be provided with all of the necessary protective devices to prevent personal injury.

(d) Proper individual conduct in case of an emergency.

(e) Methods of properly handling the various types of hydrofluoric acid containers, including approved methods for moving and emptying cylinders, barrels, carboys, drums, etc., and tank cars, and approved procedures for cleaning pipes, storage tanks and pits.

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Personal Protective Equipment. Personal protective equipment should not be used as a substitute for good safe working conditions. The correct usage of personal protective equipment requires education of the worker in the proper employment of the materials available to him. The use of proper protective equipment requires careful and constant supervision. Personal protective equipment must always be readily accessible and in good condition. It should be inspected frequently to insure usability. In addition to protective equipment, magnesium sulfate (Epsom salt), alcohol, ice, and facilities capable of supplying copious quantities of flowing water should be readily accessible at all times as the delay in acquiring these materials in case of personal injury may mean permanent injury or even a fatality to the employee.

Employees who handle hydrofluoric acid should be provided with the following equipment:

(a) Protective clothing.

(b) Suitable gas tight chemical safety goggles.

(c) Rescue harness and life line for those entering a tank or enclosed storage space.

(d) Proper respiratory protective devices. Air line masks with the proper reducing valve and filter suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply; or self-contained breathing apparatus with stored oxygen or air, which allows greater mobility but requires more highly trained men. In tank work small manholes may make this apparatus unsuitable because of its bulk, although the type known as self-generating is specially designed for entrance and egress through small openings. Masks and breathing apparatus should be approved for this purpose by the United States Bureau of Mines and should be equipped with full face pieces.

(e) Industrial gas masks equipped with canisters should be used only when it is certain that the concentration of vapor is less than 2% by volume (20,000 parts per million) and the oxygen content is not less than 16%, and then only for exposures not exceeding one-half hour. These masks should not be used in an emergency.

CAUTION: Creams or ointments should not be depended upon to afford protection.

FLUORIDATED PUBLIC WATER SUPPLIES

The foundation for the present-day addition of fluorine compounds to public drinking water supplies was laid by Churchill (94) who discovered that the cause of the mottling of teeth of people living in certain areas of the United States was the content of fluorides in the drinking water. Investigation of the phenomenon also led to the recognition that trace concentrations of fluorides in drinking water controlled caries in teeth of those using such water. It has been assumed, and evidence suggests (95), that the addition of fluoride to a water supply will produce the same effects as a water naturally containing fluoride.

Domestic water supplies have been classified (96) on the basis of dental health as (a) those carrying naturally the optimal concentration of fluorine, that is,

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about 1 p.p.m., no treatment being required; (b) those carrying an excessive concentration, requiring the removal of the excess to protect the population against endemic dental fluorosis; and (c) those deficient in fluorine to which fluorides might be added to bring the concentration to the optimal to lessen the amount of dental decay in the community.

Fluoridation means adding controlled amounts of sodium fluoride - a salt form of fluorine - to water at the rate of 1 drop for every million drops of water. It is the adjustment of the fluoride content to a tooth-beneficial level. There is no change in the taste, odor, or color of water from the added fluoride. It costs from 5 to 15 cents per person per year (97).

Health studies find this content of fluoride reduces tooth decay among children by 35 to 65 percent. The fluoride makes maturing teeth more resistant to decay - but just how it works is not clear yet. It takes a few years for the good effects to appear. There is also little evidence that fluoridation gives some protection to teeth of persons who were young adults when fluoridation was begun (97).

The interest in water fluoridation has spread throughout the country. According to Smiley (98), from a beginning 8 years ago, 771 communities are now drinking water with controlled fluoridation (15 million residents). A recent survey by the Division of Industrial Hygiene and Safety Standards of the New York State Department of Labor (99) indicates that about 280 supplies serving about 420 communities having a total population of about 8.5 million are being fluoridated; this is in addition to approximately 3 million served by supplies naturally containing concentrations of 1.0 p.p.m. or more fluoride ion.

Smiley (98) lists five important facts that support fluoridation:

1. More than 20 years of research have established that children who drink the right amount of fluoride (1 part fluoride to 1,000,000 parts of water for Indiana) have much better and more attractive teeth than children drinking water which contains lesser amounts of fluoride. Children drinking fluoridated water (1 ppm) from birth can expect to have only one-third as many cavities as they would have had without it.

2. The benefits of fluoride-bearing water continue throughout life. Adults will not need so many fillings or extractions.

3. It is inexpensive. The cost is approximately from 10 to 20 cents per person per year, including the cost of the compound and equipment (amortized over a period of 15-20 years).

4. It is harmless. It does not affect the taste, color, odor, or hardness of water. It does not cause brittle bones, heart, kidney or liver disease nor does it cause cancer. Statistics from state and local health departments, where official records are kept, show that 3,570,000 people living in 1,152 communities where the water contains fluorides (approximately 1 ppm) live just as long and are just as healthy as people living in towns with water deficient in fluorides. The National Research Council recently issued this statement, "The margin between the optimal quantity of fluoride in drinking water which is required for maximal benefit in tooth development, and the amount which produces undesirable physiological effects is sufficiently wide to cause no concern."

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5. Fluoridation is being adopted by more and more towns every day. Beginning eight years ago, 771 communities are now drinking water with controlled fluoridation (15,000,000 residents). A similar number has plans approved.

Faber (95) reports that:

> Dental decay has been reportedly caused by acids resulting from the action of micro-organisms on carbohydrates. This action is further reported to be enzymic in nature, and it is considered that the fluoride ion acts to inhibit the activity of this enzyme. Further, the fluoride ion is the only known inhibitor which is retained for appreciable periods of time.
>
> Addition of fluoride to a public water supply has been estimated to produce the following results: (1) Six times as many children having no dental caries experience. (2) A 60 percent lower rate of tooth decay. (3) A 75 percent decrease in the loss of the first permanent molar. (4) A 90 percent reduction in tooth surface caries in the upper anterior teeth.

Heyroth (100) reports as follows:

> It is suggested that there need be no fear of acute poisoning as a result of accidental or deliberate over-fluoridation of a water supply. It is reported that the lethal dose is 50-200 mgm. of fluoride ion per kgm. of body weight in rabbits, while in human self-experiments as much as 250 mgm. of sodium fluoride has been taken in one dose without harm. Results of experiments with human beings indicates that one individual took more than 20 gm. of sodium fluoride over a period of 120 weeks without showing any radiographic evidence of changes in bone density. Man and his wife, life-long residents in a Texas district where the water contained 8 p.p.m. of fluorine, showed no osseous changes whatever.
>
> There is some evidence of endemic skeletal fluorosis occurring in India, China, and South Africa, but no cases are known in which skeletal changes have occurred in regions where there is no mottling of the teeth. There is no evidence that water-borne fluoride has been a cause of nephritis.
>
> Only when the fluorine content of a water supply exceeds 5 to 6 p.p.m. will its prolonged use give rise to detectable osseous changes, and then only in the most susceptible persons. The fluoridation of water to the 1 p.p.m. level is a procedure with an ample margin of safety.

Aside from a possible hazard to the health of those using drinking water containing fluorine, there may be a hazard connected with exposure to fluoride dust, fumes, and vapors in adding fluorine chemicals to the water supply.

Five typical installations have been studied and are described by the Division of Industrial Hygiene of the State Department of Labor and the Department of Health of New York State (99) to determine the effectiveness of currently available equipment and operating procedures in protecting operators from the hazard connected with fluoridation of water.

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Powdered or granular sodium fluoride, powdered sodium silicofluoride, granular ammonium silicofluoride (to be used only when the supply is not chlorinated), and a solution of hydrofluosilicic acid are the compounds in general use (99). The granular form of sodium fluoride and ammonium silicofluoride may be handled without producing any significant amount of dust. The powdered form of the chemical varies in particle sizes so that there is some difference in the dust-producing characteristics of the powders. The powdered material cannot be handled without producing dust, such as through the transfer of small quantities of the powder from the shipping containers to hoppers of chemical feeders. Release of irritating concentrations of fumes of hydrofluosilicic acid was not disclosed when the acid was forced into a partly covered dilution tank (99).

Although, on the basis of early tests, the idea of stopping tooth decay by dosing the water supply made a tremendous appeal to doctors and laymen alike, lately, the situation has been getting more confused everyday. Business Week (101) reports that:

> Quite a few doctors and scientists want to know just what fluorine does to the bones, to elderly people with chronic diseases, and - on a long-range basis - to teeth.
>
> Few experts have challenged the finding that the fluorine does seem to inhibit tooth decay in children. But doctors have found that, of a given amount of fluorine absorbed by the body, a much larger percentage goes into the bones than into the teeth. Granting that a small amount may be fine for the teeth, these doctors wonder whether the larger amount won't damage bone marrow. They don't yet have any research evidence to back up the theory, but they feel that the threat is serious enough to warrant further investigation.
>
> As for diseases, researchers have found that animals with certain diseases, especially of the kidney, react much more unfavorably to fluorine than do healthy animals. They reason that the same is probably true to people.
>
> Further alarm is found in statistics showing that deaths from certain causes, notably heart attacks, have increased sharply in cities where the water is fluoridated. No one attributes the deaths directly to fluorine, but scientists still think that the figures indicate a danger area that should be explored.
>
> The early research on fluorine showed that it was one of the causes of mottled, or darkened, teeth. This was blamed on too-high concentrations of the chemical. The pro-fluoridators argued that the weak concentration they favored (one part of fluorine per 1-million parts of water) could do no harm to teeth. The antis argued that, no matter how weak the concentration, continued use of the treated water would permit the body to store up dangerous quantities. In effect, the antis claim that however fine the effects may be on the teeth of children, they may be overbalanced by troubles when childhood is passed.

Arguments against fluoridation of water (95) are as follows:

(1) The water works official should avoid use of the public water supply for medication until such time as controlled experimentation periods have fully elapsed and the results have been reviewed by competent

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professional authority. (2) Even at that time other ways of treating diseases of the people than through the community water supply should be thoroughly evaluated from the economic and professional standpoints. (3) "Universal application of chemicals to water for medication should be predicated upon substantial unanimity of opinion by official medical and public health agencies on the efficacy of the treatment proposed." (4) Mass medication through the public water supply is dependent upon "complete concurrence between the officials of the water department and those of the health department. ...A few investigators do not agree that published studies prove tooth decay is due to fluoride deficiency in the chemical structure of the tooth, or to fluoride deficiency in the water supply... Some investigators have exhibited concern over the possible toxicity of fluoride in a water supply. The fluoride ion is stored in the body, in the bones, and in the teeth," although it is pointed out that ingested fluoride is excreted in the urine, there being a direct correlation between the fluoride ingested and the fluoride excreted.

The author leaves the title question unanswered, stating that the answer will be supplied in part by results of controlled studies now under way, in part by the results of any other known preventive methods or future discoveries, and in part by local considerations.

Charlotte, N. C., (97) announced in 1949 it would begin fluoridation. Complaints began pouring in, according to Dr. B. M. Bethel, city and county health officer. People complained that goldfish were dying, bath tiles being stained, teeth discolored, and they were getting heartburn and nausea. However, fluoridation "hadn't even started," he said. It was begun quietly later on, and publicly announced a month later. There were no more complaints, except from ice manufacturers who reported their ice cracked easily. This trouble was corrected.

Blakeslee (97) reported that Dr. Alfred Taylor, Biochemical Institute, University of Texas, says fluoridation is "not in the public interest" because the weight of scientific data still leaves the question open of whether such water could have harmful effects. In experiments with mice, he finds that those drinking fluoridated water and eating food free of fluorides have a shorter life span. Some humans, he says, might be more sensitive to fluorides than others.

But the American Dental Association declares that more than 20 years of scientific data "has established beyond any reasonable doubt the safety and effectiveness" of fluoridation. The ADA president, Dr. Leslie M. FitzGerald says, "not a single objection to fluoridation has withstood the test of scientific investigation" (97).

Protective Measures From Exposures to Fluoride Dust, Fumes, and Vapors

The Division of Industrial Hygiene and Safety Standards, New York State Department of Labor (99) released the following data:

The compounds in general use consist of powdered or granular sodium fluoride, powdered sodium silicofluoride, granular ammonium silicofluoride, to be used only when the supply is not chlorinated and a solution of hydrofluosilicic acid. Special studies and general experience indicate that the granular form of sodium fluoride and ammonium silicofluoride may be handled without the production

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of any significant amount of dust. Therefore, it is feasible to empty containers of these granular materials into hoppers or solution tanks without the need for special equipment for the prevention of dust.

The powdered form of the chemicals varies in particle sizes so that there is some difference in the dust producing characteristics of the powders. Sodium silicofluoride usually is produced in the form of a fine powder so as to facilitate its more rapid solution. It has been demonstrated by these and similar studies that the powdered material can be handled without the production of dust, such as through the transfer of small quantities of the powder from shipping containers to hoppers of chemical feeders. Therefore suitable equipment or procedures must be adapted which permit the emptying of the total content of 100 lb. bags, 125 pound drums or barrels of the material in one operation, without the release of dust.

Several approved procedures are available, however, for permitting this convenient handling of shipping container quantities of powdered materials without the production of dust. The procedures now in use include exhaust fans and dust filters, pneumatic suction equipment for transferring material from the shipping container into storage hoppers, and specially constructed hopper enclosures permitting the dumping of bags within the enclosure. Two of these procedures were investigated as noted above. Pneumatic conveyor equipment is costly so its use normally would be restricted to large installations.

The observations at the plant where hydrofluosilicic acid is used did not disclose the release of irritating concentrations of fumes when the acid was forced into a partly covered dilution tank. It is simple, however, to provide a tight cover fitted with a vent for the dilution tank, or to use a solution feeder to force the concentrated acid from the shipping container directly into the water supply being treated, so the acid should not be handled in open tanks, measuring vessels, etc. Experience at one of the installations indicated that a precipitate was formed when the acid was diluted with water even though the mineral content of the water was very low. Therefore, it is preferred to apply the undiluted acid, except when it can be definitely demonstrated that the available diluting water is satisfactory or that either rain water or distilled water is to be used for the purpose.

Irrespective of the type of equipment used or what chemical is being applied, so-called good housekeeping must be practiced to minimize the production of dust and exposure of the operator. For instance, if a bag of the powdered material is dropped accidentally or is broken in shipment, the resulting dust will be wide-spread and hence would be troublesome later when dust respirators are not being worn. It is essential, therefore, that any bags broken in shipment or during handling be placed on a metal tray or metal wheelbarrow so that the material can be taken immediately to the chemical feeder and emptied into the hopper of the feeder. If damage to the shipping container is not too serious it may be preferable to repair the bags or drums with suitable adhesive tape immediately after the break, so that the container may be handled and stored thereafter in a dust-free manner.

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It is also evident that if full reliance were to be placed in the use of dust respirators and rubber gloves as justification for carelessness in handling powdered material that the operator would be exposed to dust which might settle and thereafter be disturbed by drafts at a time when the respirator is not worn. Accordingly, it is necessary to utilize both dust prevention procedures and also to wear dust respirators and rubber gloves when the material is handled. Clothing may be protected from any dust on the outside of bags by using rubber aprons.

The floors surrounding chemical feeders or where chemicals are stored should be impervious and smooth so as to facilitate the use of a vacuum cleaner or wet mopping or hosing to remove any spilled material. It may be desirable, therefore, in older plants to use a sheet of metal around the chemical feeder to facilitate wet mopping, etc.

The material removed by dust filters accumulates in a drawer or tray provided for the purpose. Two trays should be purchased so that an empty one may be inserted in place after the one containing the collected powder is removed. The collected powder may then be dumped from the tray into the hopper through the opening used in the regular emptying of shipping containers. The content of bags of vacuum cleaners, likewise, should be emptied in this manner.

As a result of these studies and experience with the fluoridation of public water supplies, it has been found necessary to revise the administrative procedures previously developed by the New York State Department of Health for water fluoridation programs, and to expand the requirements as to dust control equipment to be used when powdered fluorine compounds are utilized.

BIBLIOGRAPHY

1. DAVIS, H. W. Fluorspar and Cryolite. Preprint Bureau of Mines Minerals Yearbook, 1951, 18 pp.

2. ELKINS, H. B. The Chemistry of Industrial Toxicology. John Wiley & Sons, Inc., 1950, 406 pp.

3. McBEE, E. T. Fluorine Chemistry. Ind. Eng. Chem., vol. 39, No. 3, March 1947, pp. 236-237.

4. CROSSLEY, H. E. Fluorine in Coal. III. The Manner of Occurrence of Fluorine in Coals. Jour. Soc. Chem. Ind., vol. 63, 1944, pp. 289-292.

5. _____. Fluorine in Coal. I. The Micro-Analytical Determination of Fluorine. Jour. Soc. Chem. Ind., vol. 63, 1944, pp. 280-284.

6. MELLOR, J. W. Modern Inorganic Chemistry, Longmans, Green & Co., 1918, pp. 275-281.

7. JOHNSTONE, R. T. Occupational Diseases. W. B. Saunders Co., 1941, pp. 146-153.

8. MARCOVITCH, S., and STANDLEY, W. W. A Comparison of Sodium Fluoride in the Drinking Water With Similar Levels of Cryolite in the Diet on the Fluorine Content of the Body. Jour. Nutrition, vol. 16, 1938, pp. 173-181.

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9. CHEMICAL ENGINEERING CATALOG. Condensed Chemical Dictionary. Reinhold Pub. Corp., 3d. ed., 1942, 756 pp.

10. RIEGEL, E. R. Industrial Chemistry. Reinhold Pub. Corp., 1942, p. 132.

11. DAVIS, H. W., and TROUGHT, M. E. Fluorspar and Cryolite. Bureau of Mines Minerals Yearbook, 1940, pp. 1333-1352.

12. MUDD, H. F. Fluorspar and Cryolite. Chap. in Industrial Minerals and Rocks. Am. Inst. Min. Met. Eng., 1949, pp. 381-403.

13. SIMONS, J. H. Scientific and Utilitarian Value of Fluorine Chemistry. Ind. Eng. Chem., vol. 39, 1947, pp. 238-241.

14. JACOB, J. D., REYNOLDS, D. S., and MARSHALL, H. L. Phosphate Fertilizers by Calcination Process - Volatilization of Fluorine From Phosphate Rock at High Temperatures. Am. Inst. Min. Met. Eng. Tech. Pub. 659, 1936, 14 pp.

15. WAGGAMAN, W. H. Fluorine, Devil Element. Chemistry, vol. 18, 1945, pp. 1-10.

16. TRUHAUT, RENÉ. Les Fluoroses. Leur importance en hygiène industrielle et en hygiène alementaire. Les Méthodes Analytiques applicables à leur étude. (The Fluoroses. Their Importance in Industrial and Alimentaire Hygiene. Analytical Methods Applicable to Their Study). Sedes, 99, Boulevard Saint-Michel, Paris, France, 1948, 126 pp.

17. McBEE, E. T., and others. Preparation of Fluorine - Containing Polyhaloheptanes. Ind. Eng. Chem., vol. 39, No. 3, March 1947, pp. 305-309.

18. CHEMICAL ENGINEERING. Industrial Plastics. Vol. 60, 1953, pp. 193-204.

19. GREENWOOD, D. A. Fluoride Intoxication. Physiol. Rev., vol. 20, 1930, pp. 582-616.

20. STATE OF NEW JERSEY DEPARTMENT OF HEALTH. Fluorides. Div. Ind. Health, Ind. Health Bull., vol. 3, No. 5, 1949, 13 pp.

21. MARKWITH, R. H. Fluorine and Its Compounds. Ohio Department of Health pamphlet, 1940, 13 pp.

22. EDWARDS, J. D., FRARY, F. C. and JEFFRIES, ZAY. The Aluminum Industry. Aluminum and Its Products, McGraw-Hill Book Co., 1930, 378 pp.

BUDGEN, N. F. Aluminum and Its Alloys. Sir Isaac Pitman & Sons, Ltd., London, 1933, 278 pp.

23. BRAY, J. L. Non-ferrous Production Metallurgy. John Wiley & Sons, Inc., New York, 1931, pp. 33-34 and 36-38.

24. FEIL, ANDRÉ. Le Fluorisme professionnel. Intoxication professionnel par l'acide flurhydric (Occupational Fluorism. Occupational Poisoning by Hydrofluoric Acid.) Paris Med., vol. 77, 1930, pp. 242-248.

25. GELMAN, I. (From the Obuch Institute of Occupational Diseases, Moscow.) Jour. Ind. Hyg. Toxicol., vol. 18, 1936, pp. 371-379.

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26. WEBER, H., and ENGELHARDT, W. Uber eine apparature zur Erzeugung Niedriger Staubkonzeutration. Anwendung bei der Untersuchung von Stauben aus dei Berylliumgewinnung. (Regarding an Apparatus for the Determination of Low Concentrations of Dust. Use in the Investigation of Dust from Beryllium.) Zutrlbl. Gewerbehyg., vol. 10, 1931, p. 41. (Quoted by Gelman, ref. 25.)

27. INTERNATIONAL LABOR OFFICE. Occupation and Health. Fluorine Compounds, Supplement 2, Brochure 4, September 1938, 7 pp.

28. HYSLOP, FRANCES, PALMES, E. D., ALFORD, W. C., MONACO, A. R., and FAIRHALL, L. T. The Toxicology of Beryllium. U S. Public Health Service, Nat. Inst. Health, Bull. 181, 1943, 56 pp.

29. SHILEN, J., GALLOWAY, A. E., and MELLOR, J. F. Beryllium Oxide From Beryl - Health Hazards Incident to Extraction. Ind. Med., vol. 13, 1944, pp. 464-469.

30. VORWALD, A. J. (Editor). Pneumoconioses. Beryllium Bauxite Fumes. Six Saranac Symposium. Paul B Hoeber, Inc., 1950, 659 pp.

31. WILLIAMS, C. R. Atmospheric Contamination From the Casting of Magnesium. Jour. Ind. Hyg. Toxicol., vol. 24, 1942, pp. 277-280.

32. LARGENT, E. J. and FERNEAU. Exposure to Fluorides in Magnesium Foundry. Jour. Ind. Hyg. Toxicol., vol. 26, 1944, pp. 113-116.

33. BOWLER, R. G., BUCKELL, M., GARRAD, J., HILL, A. B., HUNTER, D., PERRY, K. M. A., and SCHILLING, R. S. F. The Risk of Fluorosis in Manganese Foundries. British Jour. Ind. Med., vol. 4, No. 4, October 1947, pp. 217 and 222.

34. GERHOLD, C. G., IVERSON, J. O., NEBECK. H. J., and NEWMAN, R. J. The Development of the Hydrogen Fluoride Alkylation Process. Pet. Ref., vol. 22, 1943, pp. R. 146-R. 155.

35. IPATIEFF, V. N., and PINES, H. United States Patent 2,236,099. (Quoted by Gerhold, et al, ref. 34.)

36. GROSSE, A. V., and LINN, C. B. United States Patent, 2,267,730. (Quoted by Gerhold, et al, ref. 34.)

37. OIL AND GAS JOURNAL. Catalytic Refining of Aviation Fuels. Vol. 43, No. 22, Oct. 7, 1944, p. 81.

38. VAN WINKLE, MATTHEW. Aviation Gasoline Manufacture. McGraw-Hill Book Co., 1944, pp. 168-173.

39. BENSON, ROY. Hydrogen Fluoride Exposure - Prevention in the Operation of HF Alkylation Plants. Ind. Med., vol. 13, 1944, pp. 113-117.

40. SIMONS, J. H. Fluorocarbon Background. Chem. Eng., vol. 56, 1949, p. 107.

41. DRINKER, P., and NELSON, K. W. Welding Fumes in Steel Fabrication. Ind. Med., vol. 13, 1944, pp. 673-675.

42. READY, N. E. Fluoride Vapors and Dust. California Safety News, vol. 27, 1943, p. 13.

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43. WOLFE, W. A., and KERR, E. G. The Composition of Human Bone in Chronic Fluoride Poisoning. Am. Jour. Med. Sci., vol. 195, 1939, pp. 493-497.

44. ROCKWOOD, N. C. Cement Plant Making "Bone Meal." Rock Prod., vol. 47, 1944, pp. 44-47.

45. OIL, PAINT, AND DRUG REPORTER. Phosphate Rock Feed. Vol. 146, 1944, p. 7.

46. _____. Fluorine Spray Residue Limit to be Set. Vol. 146, 1944, p. 36.

47. VOEGTLIN, CARL, and HODGE, H. C. Pharmacology and Toxicology of Uranium Compounds, With a Section on the Pharmacology and Toxicology of Fluorine and Hydrogenfluoride. McGraw-Hill Book Co., Inc., vols. 1 and 2, 1949, 1,084 pp.

48. SAX, N. I. (assisted by M. J O'Herin and W. W. Schultz). Handbook of Dangerous Materials. Reinhold Pub. Corp., 1951, 848 pp.

49. ROHOLM, K. Fluorine Intoxication - A Clinical-Hygienic Study With a Review of the Literature and Some Experimental Investigations. London, 1937, 364 pp.

50. DE EDS, F. Chronic Fluorine Intoxication. A Review. Medicine, vol. 12, 1933, pp. 1-60.

51. OST, H. Der Kampf gegan schädliche Industriegase. (The Fight Against Harmful Industrial Gases.) Ztschr. für Angew. Chem., vol. 20, 1907, pp. 1689-1693.

52. CAMERON, C. A. On the Toxicity of Silicon Fluoride. Dublin Jour. Med. Sci., vol. 83, 1887, p. 20.

53. VAN LEEUWEN, W. S. Die Nebelkatastrophe in Industriegebiet südlich von Lüttich. (The Fog Catastrophy in the Industrial District South of Lüttich.) Münch. Med. Wochnschr., vol. 78, 1931, p. 49.

54. FENNER, G. Zur Nebelkatastrophe in Industriegebiet südlich von Lüttich. (Regarding the Fog Catastrophy South of Lüttich.) Chem.-Ztg., vol. 55, 1931, pp. 69-70.

55. ROHOLM, K. The Fog Disaster in the Meuse Valley, 1930. A Fluorine Intoxication. Jour. Ind. Hyg. and Toxicol., vol. 19, 1937, pp. 126-137.

56. JOURNAL AMERICAN MEDICAL ASSOCIATION. Industrial Pollution of Human Environment. Vol. 140, 1949, p. 1342.

57. BUSINESS WEEK. Donora Deaths. Dec. 4, 1948, p. 28.

58. PUBLIC HEALTH SERVICE. Air Pollution in Donora, Pa. Epidemiology of the Unusual Smog Episode of October 1948. Preliminary Report. P. H. Bull. 306, 1949, 173 pp.

59. MØLLER, P. F., and GUDJONSSON, SK. V. Massive Fluorose der Knochen und Bander (Fluorose bei Kryolitharbeitern). (Massive Fluorosis of the Bones and Ligaments.) Reichsarbeitsblatt, vol. 13 (NF), 1933, p. III 265. (Quoted by Roholm, ref. 55.)

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60. SLAGSVOLD, L. Fluoroforgiftning. (Fluorine Poisoning) Norsk Vet. - Tidsskr., vol. 46, 1934, p. 2. (Quoted by Roholm, ref. 55.)

61. LILLEENGEN, K. Mikroskopisk undersologelse av benpreparater fra sauer lidende av kronisk fluorforgiftning. (Microscopic Examination of Bone From Sheep Suffering From Chronic Fluorine Poisoning.) Norsk Vet. - Tidsskr., vol. 46, 1934, p. 68. (Quoted by Roholm, ref. 55.)

62. BARDELLI, P., and MENZANI, C. Ricerche sulla fluorosi spontanea dei ruminanti. Nota Preventiva. (Research on Spontaneous Fluoroses of Ruminantia Preventive Note.) Ann. d'Ingen., vol. 45, 1935, p. 399. (Quoted by Roholm, ref. 55.)

63. BLACK, G. V., and McKAY, F. S. Mottled Teeth: An Endemic Developmental Imperfection of the Enamel of the Teeth Heretofore Unknown in the Literature of Dentistry. Dental Cosmos., vol. 58, 1916, pp. 129, 627, 781, and 894. (Quoted by Roholm, ref. 55.)

64. McCLURE, F. J. A Review of Fluorine and Its Physiological Effects. Physiol. Rev., vol. 13, 1933, pp. 277-297.

65. VELU, H. La Darmous (ou Dermes). Arch. inst., Pasteur Algérie, vol. 10, 1932, 41 pp.

66. KAMINSKI, ARTHUR. Über Schädigungen der Zähne und des Mundes in der Glasindustrie und Berucksichtigen der übrigen gewerblichen Schädigungen. (Regarding Injuries to Teeth and the Mouth in the Glass Industry and Reference to the Remaining Industrial Injuries.) Inaug. Dissertation for Doctor of Dentistry. Breslau. 1928, 26 pp.

67. AGATE, J. N. (and other members of the Committee). Industrial Fluorosis. Med. Res. Council Memo. 22, H.M.S.O., London, 1949, 131 pp.

68. WILLIAMSON, M. M. Endemic Dental Fluorosis in Kenya: Preliminary Report. East African Med. Jour., vol. 30, 1953, pp. 217-266; ab. Jour. Am. Med. Assoc., vol. 153, 1953, p. 1128.

69. MASSEY, L. M. Similarities Between Disease Symptoms and Chemically Induced Injury to Plants. Chap. in Air Pollution, McGraw-Hill Book Co., Inc., 1952, pp. 48-51. Pres. at U. S. Tech. Conf. on Air Pollution, Agricultural Panel, Washington, D. C., May 3-5, 1950.

70. MACINTIRE, W. H. Air Versus Soils as Channels of Fluoric Contamination of Vegetation in Two Tennessee Locales. Chap. in Air Pollution, McGraw-Hill Book Co., Inc., 1952, pp. 53-57. Pres. at U. S. Tech. Conf. on Air Pollution, Agricultural Panel, Washington, D. C., May 3-5, 1950.

71. DAINES, R. H., LEONE, I., and BRENNAN, E. The Effect of Fluorine on Plants as Determined by Soil Nutrition and Fumigation Studies. Chap. in Air Pollution, McGraw-Hill Book Co., Inc., 1952, pp. 97-105. Pres. at U. S. Tech. Conf. on Air Pollution, Agricultural Panel, Washington, D. C., May 3-5, 1950.

72. GRIFFIN, S. W., and BAYLES, B. B. Some Effects of Fluorine Fumes on Vegetation. Chap. in Air Pollution, McGraw-Hill Book Co., Inc., 1952, pp. 106-114. Pres. at U. S. Tech. Conf. on Air Pollution, Agricultural Panel, Washington, D C., May 3-5, 1950.

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73. PEIRCE, A. W. Chronic Fluorine Intoxication in Domestic Animals. Nutrition Abstracts and Reviews, University of Adelaide, Adelaide, Australia, vol. 9, 1939, 14 pp.

74. BLAKEMORE, F., BOSWORTH, T. J., and GREEN, H. H. Industrial Fluorosis of Farm Animals in England, Attributable to the Manufacture of Bricks, the Calcining of Ironstone, and to Enamelling Processes. Jour. Comp. Path. Therapeut., vol. 58, 1948, pp. 267-291.

75. McNALLY, W. D. Toxicology. Industrial Medicine Pub. Co., Chicago, 1937, pp. 91-108.

76. SOLLMANN, T. A Manual of Pharmacology. W. B. Saunders Co., Philadelphia, 1940, pp. 853-855.

77. MØLLER, P. F. Fluorine Poisoning, Seen from Röntgenological Standpoint. Brit. Jour. Rad., vol. 12, 1939, pp. 13-20.

78. AST, D. B. The Caries - Fluorine Hypothesis and a Suggested Study to Test Its Application. Public Health Reports, vol. 58, 1943, pp. 857-879.

79. McKAY, F. S. Mottled Enamel. The Prevention of Its Further Production Through a Change of Water Supply at Oakley, Idaho. Jour. Am. Dental Assoc., vol. 20, 1933, p. 1137. (Quoted by Ast, ref. 78.)

80. CHURCHILL, H. V. Occurrence of Fluorides in Some Waters of the United States. Jour. Ind. Eng. Chem., vol. 23, 1931, p. 996. (Quoted by Ast, ref. 78.)

81. SMITH, M. C., LANTZ, E. M., and SMITH, H. V. The Cause of Mottled Enamel, a Defect of Human Teeth. Univ. Arizona, College of Agric., Agric. Exp. Sta. Tech. Bull. 32, 1931. (Quoted by Ast, ref. 78.)

82. BALOZET, L., and VELU, H. Bull. soc. path. exotique, vol. 24, 1931, p. 848. (Quoted by Ast, ref. 78.)

83. LINSMAN, J. F., and McMURRAY, C. A. Fluoride Osteosclerosis From Drinking Water. Radiology, vol. 40, 1943, pp. 474-483.

84. LARNER, JOSEPH. Toxicological and Metabolic Effects of Fluorine-Containing Compounds. Ind. Med. Surg., vol. 19, 1950, pp. 535-539.

85. MURRAY, M. M., and WILSON, D. C. Fluorine Hazards: With Special Reference to Some Social Consequences of Industrial Processes. Lancet, Dec. 7, 1946, pp. 821-825; p. 835, Fluorosis - Endemic and Man Made; ab. Bull. Hyg. (London), vol. 22, 1947, pp. 257-258.

86. BRANDL, J., and TAPPEINER, H. Ueber der Ablagerung von Fluorverbindungen im Organismus Nach Fütterung mit Fluornatrium. (Regarding the Deposition in the Organism of Fluorine Compounds After Feeding With Sodium Fluoride.) Ztschr. Biol., vol. 28, 1891, p. 518. (Quoted by Roholm, ref. 55.)

87. FAIRHALL, L. T. Industrial Toxicology, Williams and Wilkins Co., 1949, pp. 79-80.

88. JOHNSTONE, R. F. Occupational Medicine and Industrial Hygiene. C. V. Mosby Co., St. Louis, Mo., 1948, pp. 187-189.

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89. MACHLE, W., THAMANN, F., KITZMILLER, K., and CHOLAK, J. The Effects of the Inhalation of Hydrogen Fluoride: I. The Response Following Exposure to High Concentrations. Jour. Ind. Hyg., vol. 16, 1934, pp. 129-145.

90. MACHLE, W., and KITZMILLER, K. The Effects of the Inhalation of Hydrogen Fluoride. II. The Response Following Exposure to Low Concentrations. Jour. Ind. Hyg., vol. 17, 1935, pp. 223-240.

91. PATTY, F. E. Industrial Hygiene and Toxicology. Intersci. Pub., Inc., New York, vol. 2, 1949, pp. 542-544.

92. MANUFACTURING CHEMISTS' ASSOCIATION, INCORPORATED. Hydrofluoric Acid. Chemical Safety Data Sheet SD-25, adopted 1948.

93. MACHLE, W., and EVANS, E. E. Exposure to Fluorine in Industry. Jour. Ind. Hyg. and Toxicol., vol. 22, 1940, pp. 213-217.

94. H. V. CHURCHILL. Fluorides and Mottled Enamel. Chem. Eng. News, vol. 27, 1949, p. 3867.

95. FABER, H. A. Shall Fluoride Be Added to Public Water Supplies. Water & Sewage Works, vol. 95, 1948, pp. 393-400; abs. Public Health Eng. Ab., vol. 30, 1950, pp. 25-26.

96. DEAN, H. T. Fluorine and Dental Caries. Am. Jour. Othodontics Oral Surg., vol. 134, 1947, p. 49.

97. BLAKESLEE, ALTON L. Fluoridation is Gaining Speed in U. S., But So Is Its Opposition. Washington Star, Washington, D. C., Jan. 3, 1954, p. A-31.

98. SMILEY, R. D. Excuse Our Dust. Indiana State Board of Health, vol. 56, 1953, pp. 60 and 66.

99. DIVISION OF INDUSTRIAL HYGIENE AND SAFETY STANDARDS. Dust Control Procedures in the Fluoridation of Public Water Supplies in New York State., New York State Dept. of Labor, vol. 32, 1953, pp. 21-24 and 27-28.

100. HEYROTH, F. F. Toxicological Evidence for the Safety of the Public Water Supplies. Am. Jour. Pub. Health, Dec. 1952, vol. 42, No. 12, pp. 1568-1575; abs. Bull. Hyg., June 1953, vol. 28, No. 6, pp. 443-444.

101. BUSINESS WEEK. What Should a City Do to Its Water? March 21, 1953, pp. 66-67.

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